

ORGANIC CHEMISTRY OF BIVALENT SULFUR

VOLUME I

by

E. EMMET REID, M.A., Ph.D., LL.D.

*Professor of Chemistry, Emeritus
Johns Hopkins University*



1958

CHEMICAL PUBLISHING CO., INC.

212 Fifth Avenue, New York, N. Y.

© 1958

CHEMICAL PUBLISHING CO., INC.

New York

N. Y.

Printed in the United States of America

Chemistry
Library

QD
412
S1P2

v. 1

Foreword

In 1925, when the American Petroleum Institute set up its original program of fundamental research, one of the projects was assigned to Dr. E. Emmet Reid at the Johns Hopkins University. It dealt with sulfur compounds found in petroleum. Doctor Reid has continued his work in the field of organic sulfur compounds throughout a long and productive career. Today he is a widely recognized authority in this area.

In the early days of petroleum refining in this country sulfur compounds were not a great problem, except for the odor of mercaptans in kerosene and gasoline. The adoption of high-temperature distillation and cracking processes emphasized the corrosive properties of sulfur and its compounds. The detrimental effects of many sulfur compounds on the potency of tetraethyllead added to gasoline arouses deep interest today in the chemistry of sulfur compounds in petroleum.

Organic sulfur compounds occur in practically all living matter, some rather simple, e.g., the protective fluid ejected by *Mephitis mephitis*, others quite complex, such as most proteins. The synthesis and uses of these essential organic sulfur compounds is a broad field that is seldom touched by the average organic chemist. Without this treatise the researcher in the field of organic sulfur compounds would need to spend many additional hours searching the literature for essential data.

The appearance of this work by Doctor Reid at this time is, therefore, particularly timely. Everyone interested in the refining of petroleum, as well as those working in related fields, will welcome such an authoritative and comprehensive treatise on this very important subject.

CARY R. WAGNER

Table of Contents

<i>Chapter</i>	<i>Page</i>
1. MERCAPTANS	15
Introduction	
Occurrence of Mercaptans	
Preparation of Mercaptans	
By Addition of Hydrogen Sulfide to Unsaturates	
From Esters of Inorganic Acids	
From Alkyl Halides and Metal Sulphydrates	
By Hydrolysis of a Thioester	
Thioacetates	
Thiocarbonates and Thiocarbamates	
Bunte Salts	
From Thiourea	
By Reduction	
Disulfides	
Other Reductions	
By the Grignard Reaction	
Catalytic Formation of Mercaptans	
Miscellaneous Formations	
Dimercaptans or Dithioglycols	
Comparisons of Mercaptans with Alcohols, Hydrocarbons, and Alkyl Halides	
Physical Properties of Mercaptans	
2. REACTIONS OF MERCAPTANS	107
Introduction	
Formation of Addition Compounds	
Decomposition of Mercaptans	
By Various Agents	

<i>Chapter</i>	<i>Page</i>
2. REACTIONS OF MERCAPTANS—Continued	107
Thermal Decomposition	
Desulfurization by Hydrogenation	
Oxidation	
By Oxygen	
By Oxidising Agents	
By Halogens	
Formation of Mercaptides	
Ammonium Mercaptides	
Alkali Mercaptides	
Removal of Mercaptans by Alkaline Extrac- tion	
Solutizers	
Regeneration of Wash Liquors	
Heavy Metal Mercaptides	
Mercury	
Copper	
Cadmium and Zinc	
Silver	
Iron, Nickel, and Cobalt	
Antimony and Bismuth	
Gold, Platinum, and Palladium	
Other Metals	
Lead Mercaptides	
The "Doctor" Treatment	
Physical Methods of Removal of Sulfur Com- pounds	
Solvent Extraction	
Desulfurization by Adsorbents	
Desulfurization by Freezing	
Segregation by Distillation	
The Detection of Mercaptans	
Estimation of Mercaptans	
Identification of Mercaptans	
Physiological Effects	
Uses of Mercaptans	
As Intermediates	
As Odors	
As Antioxidants and Inhibitors	

<i>Chapter</i>	<i>Page</i>
2. REACTIONS OF MERCAPTANS—Continued	107
As Pesticides	
In Flotation	
Miscellaneous Uses	
3. NEGATIVE DERIVATIVES	262
General	
Sulfenic Acids and Derivatives	
Sulfenyl Halides, RSX	
Formation	
Sulfenyl Thiocyanates	
Reactions	
Oxidation and Reduction	
With Hydrogen Sulfide and Mercaptans	
With Metallic Salts	
Addition to Unsaturation	
Miscellaneous	
Disulfide Chlorides, RSSCl and ArSSCl	
Sulfenamides, RSNH ₂ , RSNHR', RSNR'R''	
Formation	
Properties	
Reactions	
With Acids	
Oxidation and Reduction	
With Aldehydes and Ketones	
Rearrangement	
Sulfenic Esters, RS·OR'	
Formation	
Properties	
Reactions	
Sulfenic Anhydrides, RS·O·SR	
Perchlormethylmercaptan, Cl ₃ CSCl	
Formation	
Properties	
Reactions	
Reduction	
With Amines	
Applications	
Esters of Thionitrous and Thionitric Acids	

<i>Chapter</i>	<i>Page</i>
3. NEGATIVE DERIVATIVES—Continued	262
Trithiophosphites	
Thioarsenious Esters	
Trithioantimonites	
Bismuth Compounds	
Thioboric Esters	
Thiophosphoric Esters	
Formation	
Amid-Esters	
The Reaction of Phosphorus Pentasulfide with an Alcohol	
Phosphorus Pentasulfide and Other Compounds	
Alkyl and Aryl Phosphine Derivatives	
Parathion	
Physical Properties of Thiophosphosphoric De- rivatives	
Ester-Halides	
Esters	
Amides	
Acid-Esters and Derivatives	
Melting Points of Some Salts	
Ester-Anhydrides and Ester-Sulfides	
Alkyl Phosphorus Compounds	
Tetrathioorthoesters	
Tetrathioorthocarbonates, $C(SR)_4$	
Tetrathioorthosilicates, $Si(SR)_4$	
Properties of Tetraalkyltetrathio-Orthosilicates	
Some Mixed Silicon Compounds	
Tetrathiostannates, $Sn(SR)_4$	
Tetrathiogermanates, $Ge(SR)_4$	
Alkyl Thiosulfates	
Reactions of Alkyl Thiosulfates	
Esters of Thiosulfonic Acids	
Thiosulfinic Esters	
Thiosulfite Esters	
4. SUBSTITUTED MERCAPTANS	376
Hydroxymercaptans	
Hydroxymethyl-Mercaptan and Derivatives	

<i>Chapter</i>	<i>Page</i>
4. SUBSTITUTED MERCAPTANS—Continued	376
Hydroxethyl-Mercaptan	
Haloethyl-Mercaptans	
Alkoxyethyl-Mercaptans	
Other Hydroxy-Mercaptans and Derivatives	
Thioglycerols	
BAL	
Pharmacology of BAL	
1-Thiosorbitol	
Aromatic Hydroxy-Mercaptans	
Aldehydo-Mercaptans	
Keto-Mercaptans	
Thiosaccharides	
Thioses	
Synthesis of Glucothiose	
Thioglycoses	
Sulfide-Mercaptans	
Aminomercaptans	
Formation	
Reactions	
Applications	
Mercapto-Sulfonic Acids	
Physical Properties	
Hydroxy-Mercaptans	
Ether Mercaptans	
Halo-Mercaptans	
Sulfide-Mercaptans	
Aldehyde and Keto-Mercaptans	
Amino-Mercaptans	
Aromatic Mercaptans	
Miscellaneous Mercaptans	
5. MERCAPTO-ACIDS	436
Thioglycolic Acid	
Thiolactic Acid	
β -Mercaptopropionic Acid	
Mercaptobutyric Acids	
Mercaptovaleric Acids	
Higher Mercapto-Acids	

<i>Chapter</i>	<i>Page</i>
5. MERCAPTO-ACIDS—Continued	436
Dimercapto-Acids	
Dibasic Acids	
Aromatic Mercapto-Acids	
Amino-Mercapto-Acids	
Cysteine	
Homologs and Analogs	
Penicillamine	
Synthesis	
Reactions	
Ergothioneine	
Physical Properties of Mercapto-Acids	
Monobasic Mercapto-Acids	
Dimercapto-Acids	
Dibasic Mercapto-Acids	
Aromatic Mercapto-Acids	

Acknowledgments

Publication of this work was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

It is a pleasure to express my gratitude also to the Freeport Sulphur Company for their grant.

Introduction

One hot summer day in 1894, I was reading Remsen's Organic Chemistry and came across the statement that mercaptan is the analog of alcohol. Curiously enough I remember, as if it had been yesterday, just where I was sitting on a Louisiana porch when I read this. One hot summer day fifteen years later I was reading theories of esterification and pondering the question whether the oxygen in the molecule of water that is eliminated comes from the alcohol or from the acid. The analogy of mercaptan to an alcohol came back to me and I decided to try the esterification of mercaptan. So off to the laboratory I went to prepare 1400 grams of ethyl mercaptan. The only other person working in the laboratory was the janitor, who had no sense of smell. I found that the esterification of mercaptan by an acid gives the thioester which can be hydrolyzed back to the mercaptan and acid. Several years later, with the aid of students, the esterification of mercaptans was taken up in a broad way. In 1958, I am still working on mercaptans.

In World War I, some one had the idea that butyl mercaptan might be used as a camouflage gas and I was asked to work out a process for making it. A small plant was put up at the American University in Washington and a ton of the product was shipped to France. There is no record of its fate, though it should have been possible to trace it.

When the American Petroleum Institute received money for research pertaining to petroleum, a project on the preparation of a series of mercaptans and a study of their reactions was placed in the Johns Hopkins Chemical Laboratory. The first stage was an extensive literature search. This showed the need for a comprehensive review of the organic chemistry of sulfur.

Of all the serious mistakes of my life, the most expensive both

in labor and money, was undertaking to write a monograph on organic sulfur compounds. Thirty years ago, when there was little interest in the subject, this might have been possible. I made slow progress working alone. In 1939 the Freeport Sulfur Company gave me a generous grant for assistance. This was a big boost, but when the money had been spent I found that I had grossly underestimated the task and that the major part of it remained to be done. I had passed the point of no return and had to go ahead with my own resources. When the manuscript was at last written and typed I found it so out of date that it had to be rewritten. Now it should be rewritten again but, by the time this could be done, it would be more outdated than it is now. Organic chemistry has been expanding at a breath-taking rate but the rate is twice as fast in the sulfur sector as in the whole. Of the 36,000 compounds in the formula index of *Chemical Abstracts* for 1954, about one third contain sulfur, while in 1924 these were only one sixth. Keeping up with organic sulfur chemistry is hopeless. The coverage is less complete and the discussion less adequate than I had hoped to make them. The fascinating, but intricate, biochemistry of sulfur has had to be left to specialists in that field. However, the book does contain much information and its twenty thousand references will serve as first aid in literature searches.

Earlier articles in English, German, French, and Italian were read in the original, but in recent years dependence has had to be put on *Chemical Abstracts* which has been searched through 1954 for the first three volumes and through 1957 for the last two.

Without the impetus of the grant from the Freeport Sulphur Company the project might have been abandoned in its early stages; without the recent support of the Petroleum Research Fund of the American Chemical Society it could not have been completed.

There is not sufficient space to name the many chemists to whom gratitude is due for help of various kinds. I am glad to acknowledge my indebtedness to Dr. Jane Dick Meyer, who spent many months of patient labor on the manuscript. Without her efficient help the book could not have been brought to completion. Thanks are due to Dr. J. C. Patrick, to Dr. E. M. Fettes, and to others of the Thiokol Chemical Corporation for their assistance, and to Dr. G. Nathan Reed and Dr. Norman Donaldson for capable indexing.

CHAPTER 1.

Mercaptans

Introduction

An early chemist compared the preparation of a new alcohol to the discovery of a new metal. Starting with a metal one can prepare a long series of compounds, oxide, hydroxide, sulfide, chloride, nitrate, sulfate, etc., paralleling those of other metals. Similarly, from a new alcohol a long series of compounds can be prepared, a chloride, a bromide, an iodide, and a host of esters. Methyl and ethyl compounds are far more numerous than are the salts of sodium and potassium. When Zeise discovered mercaptan, he did not start just one series of compounds but opened up a whole section of organic chemistry. Many mercaptans have been made and many more can be; for each alcohol a sulfur analog is possible. From these an endless number of derivatives can be prepared. The importance of mercaptans and other sulfur compounds is just beginning to be realized.

The chemistry of organic sulfur compounds centers around mercaptans. They are the analogs of the alcohols and are spoken of as thioalcohols, thiols, or alkanethiols. The $-SH$ group as a substituent in a hydrocarbon is called mercapto, which corresponds to hydroxy. Thus CH_3SH may be called mercapto-methane and $HSCH_2COOH$, mercapto-acetic acid. The name mercaptum was given by Zeise to the group C_2H_5S- which is taken up by the mercury from corpus mercurio captum and

mercaptan to C_2H_5SH which captures the mercury from corpus mercurium captans.^{469, 685} The formation of the mercury derivatives was a striking characteristic. Zeise recognized the analogy to alcohol which was further elaborated by Liebig.^{387a} Interesting accounts of Zeise and his discoveries are given by Diergart¹⁶¹ and O. Zeise.⁶⁸⁴ An excellent review of mercaptan chemistry has been written by Malisoff, Marks, and Hess.⁴⁰⁷

Occurrence of Mercaptans

Alcohols, either free or as esters, are found in natural products in great variety and in large amounts, but the mercaptans rarely appear. Three alcohols, geraniol, citronellol, and phenylethyl alcohol are the chief constituents of attar of roses but the mercaptans are at the other end of the odor scale. A butyl mercaptan is used by the skunk as a defense weapon.^{48, 197} The lower mercaptans are noted for their powerful and disagreeable odors. As little as 0.000,000,002 mg. of ethyl mercaptan, or 1 part in 50,000,000,000 of air, can be detected by its odor.²⁰⁵ The odor is strong at 0.6 parts per million, distinct at 0.03 to 0.07 and detectable at 0.002.⁶¹¹ In very high concentrations the bad odor vanishes and is replaced by one somewhat like that of chloroform.^{506b} The odor diminishes as the carbon chain lengthens; nonanethiol-2 is not unpleasant and those above lauryl are practically odorless.

Commercial quantities of methyl mercaptan are extracted from the "sour gas" of West Texas. Some ethyl mercaptan is also present.

Methyl mercaptan, apparently present in the free state, has been isolated from the roots of *Raphanus sativus*, 0.31 g. from 40 kg. of the fresh roots.⁴³⁸ Traces are found in some leaves³⁵⁵ and even in foods.³⁴⁷ Methyl mercaptan and isopropyl mercaptan are in eucalyptus.⁵⁰⁸ *Schizophyllum commune* Fr., a wood-rotting fungus, liberates methyl mercaptan when grown on a synthetic medium containing inorganic sulfates.⁷⁰ It is liberated when keratin is heated to 150° * with steam.⁴² It is formed in the anaerobic fermentation of gelatin and albumin and in the putrefaction of proteins.^{354, 443a, 443c, 444, 523, 529a, 552} It is among the products of the action of trypsin on proteins.²⁵⁰ Methyl mercaptan

* All temperatures in this book are given in degrees Centigrade, unless otherwise stated.

was obtained by fusing proteins with potassium hydroxide. Egg albumin gave 0.35%, the maximum amount.⁵⁶¹ Either acid or alkaline hydrolysis of wool produces some methyl mercaptan.⁵³⁰ After asparagus is eaten, methyl mercaptan appears in the urine within an hour.^{443b} The urine of several people who had eaten 12 kg. of asparagus was distilled and the mercaptan caught in mercuric chloride solution.^{234, 443c} Ethyl mercaptan is found in the urine of rabbits fed on cabbage.^{529b} Distillation of the urine of various animals gives hydrogen sulfide and mercaptans.⁴⁸⁵ Mercaptans are found in hydrolyzed snake venoms.⁴²⁴ The lower mercaptans are split off in the cooking of animal and vegetable foods and are found in feces.⁴⁴⁸ Methyl mercaptan may be produced by the bacterial decomposition of urine.³²⁷

Some allyl mercaptan accompanies the allyl disulfide in oil of garlic.⁵⁹⁰ Propyl mercaptan is evolved from freshly chopped onions.¹¹⁵

Swartz, working in Wöhler's laboratory, separated the secretion of the skunk, *Mephitis texana*, into fractions boiling 105 to 111° and 192 to 200°. ⁶⁰⁰ A sulfur compound which gave precipitates with heavy metal salts was separated from the same secretion.³⁹²

The formation of ethyl mercaptan has been observed in vinous fermentation but this is supposed to be due to the reaction of the ethanol with sulfur or sulfur compounds present under the influence of the enzymes.^{410, 413} The probability that alcohols are formed by the reduction of aldehydes in fermentations raised the question as to whether mercaptans can be produced by the reduction of thioaldehydes. Experiment showed that thialdin (used as a substitute for the insoluble trimeric thiacetaldehyde) added to an actively fermenting sugar solution is transformed into mercaptan.^{445, 446} Butyraldehyde and *i*-valeraldehyde mixed with alcoholic ammonium sulfide yield the corresponding mercaptans.⁴⁵¹ The bad odor of fermentation alcohol is attributed to mercaptan similarly formed.^{123, 192} Alkyl disulfides are reduced to the mercaptans in bread cultures of *Penicillium brevicaulis*.^{72, 115, 118} In the making of wood pulp, methyl mercaptan is given off but nothing is known as to how it is formed.^{56, 193, 245, 522} Its recovery has been proposed.^{447, 517} Methyl and ethyl mercaptans are found in illuminating gas.^{104, 297, 304, 338, 436, 671} Mercaptans are in coal tar.^{404b, 542, 543}

Mercaptans appear in petroleum distillates, but in most cases it is certain that they were not present as such in the original oils. They may have been split off from larger molecules containing RS- groups, or they may have been formed by the union of hydrogen sulfide and unsaturates under the high pressures and temperatures prevailing in cracking stills.^{19, 69, 71, 114, 117, 121, 136, 166, 179, 189, 210, 218, 232, 258, 259, 314, 328, 409, 439a, 473, 563, 680} It has been suggested that mercaptans may be formed by the union of hydrogen sulfide with unsaturates in the acid treatment of naphthas.^{659, 660}

The chief mercaptan present in petroleum distillates is ethyl. The next is probably methyl. Propyl,^{68, 271} *i*-propyl,^{68, 69, 271} butyl,^{68, 271} *i*-butyl,^{69, 271} *s*-butyl^{271, 439b} and *t*-butyl²⁷¹ mercaptans have been identified.²⁶⁴ Higher mercaptans are present, but the amounts taper off as the molecular weights go up. Some naphthas of West Texas origin contain relatively large proportions of the higher, butyl to nonyl.¹⁰ Various methods of recovering these mercaptans have been proposed.^{149, 364, 400, 479, 626} Though their percentage in crude distillates is minute, the aggregate amount removed from the billions of gallons of gasoline manufactured is large. There is the possibility of recovering tank cars of mercaptans from this source. In catalytic cracking, now so widely used, a larger proportion of the sulfur of the crude is converted to hydrogen sulfide and thiophenes and less to mercaptans.

Mercaptans and hydrogen sulfide are the chief sulfur compounds in absorption gasoline from refinery still gases.⁶²⁵ Certain shale oils from Tyrol are very high in sulfur. Thiophenes account for the most of it, but there are also some mercaptans.⁷³

The subject of mercaptans and other sulfur compounds in petroleum was reviewed by Schmeling in 1936⁵³⁹ and discussed thoroughly in a symposium at the American Chemical Society meeting at San Francisco, April 1949.^{39, 134, 263, 271, 388, 587, 616, 640} The removal of mercaptans from petroleum distillates will be treated in chapter 2.

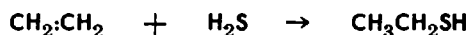
Preparation of Mercaptans

BY ADDITION OF HYDROGEN SULFIDE TO UNSATURATES

The possibilities of this method have just begun to be explored. Many unsaturates are available and hydrogen sulfide is cheaper

than reagents made from it. As there are no other products, a pound of the reactants produces a pound of mercaptan. From 109 g. of ethyl bromide and 56 g. of sodium hydrosulfide, it is theoretically possible to get 62 g. of ethyl mercaptan with 103 g. of sodium bromide as a by-product. There is a loss incident to the recovery of the mercaptan from the solvents used. The addition of 34 g. of hydrogen sulfide to 28 g. of ethylene gives the same weight of ethyl mercaptan with no by-products. With the addition method there is, however, a difficulty; the mercaptan first formed tends to combine with the unsaturate and the product may be a mixture of the mercaptan and the corresponding sulfide. A comprehensive investigation of the conditions under which the addition takes place is needed. Ultraviolet light, heat, and pressure are known to favor the addition; acids, bases, peroxides, and metal sulfides have been claimed as catalysts. There is much difference in the activity of unsaturates in taking up other addenda. Conditions can be found under which hydrogen sulfide can be added selectively to one unsaturate in the presence of others. This subject has been reviewed.^{287, 416}

Mercaptans are formed in some cases when mixtures of liquid hydrogen sulfide and unsaturates are kept at room temperature for several weeks.⁸¹ An alkene and hydrogen sulfide unite when heated together at 160°: ^{314, 323}



Cyclohexyl mercaptan is formed from cyclohexene at 150°.⁴²¹ When the double bond is activated by certain groups, as in 3,6-divinyl-2,5-diketopiperazine, addition of hydrogen sulfide may take place even at 0°.⁵⁷¹ When the reactants are passed over silica gel at 700°, addition takes place.⁴⁰⁶ The equilibrium of hydrogen sulfide and propylene over nickel carbonate on kieselguhr at 300° has been measured.^{38, 332} The results are given by the equations:

$$\begin{array}{rclclcl} i\text{-PrSH} & \Delta F & = & -14,600 & + & 28.80T \\ n\text{-PrSH} & \Delta F & = & -14,600 & + & 30.00T \end{array}$$

ΔH is 14,600 and the values for ΔF at these temperatures are:

		300°	275°	250°
<i>i</i> -PrSH	ΔF	1900	1180	460
<i>n</i> -PrSH	ΔF	2600	1850	1100

With phosphoric acid on activated carbon, propylene and hydrogen sulfide gave a maximum conversion of 17% at 200°.

With nickel on kieselguhr, ethylene showed 22% mercaptan at 250°. ^{167, 332}

Isoprene and hydrogen sulfide combine at 96° in the presence of iron sulfide to the mono- and then the dimercaptan, $(\text{CH}_3)_2\text{C}(\text{SH})\text{CH}:\text{CH}_2$ and $(\text{CH}_3)_2\text{C}(\text{SH})\text{CH}(\text{SH})\text{CH}_3$.⁷⁵ Sulfides of nickel, cobalt, and iron are said to catalyze the addition of hydrogen sulfide to *i*-butene.³ Alumina and ferric oxide also are catalysts.²⁵² Unsaturation is sulfurized by simultaneous action of hydrogen sulfide and sulfur.^{2, 214, 486} An absorptive catalyst, such as fuller's earth, silica gel,^{320b, 449, 553b, 651} or silica-alumina gel, may be used to bring about the combination.^{399, 544, 545} The use of hydrogen with titania gel is said to be beneficial.³⁶⁵ High-molecular-weight mercaptans are formed by reacting rosin or terpenes with hydrogen sulfide in the presence of acids or bases.⁴⁶⁰ Olefins react with hydrogen sulfide at room temperature in the presence of an acid, such as sulfuric,^{151, 320a, 337, 455, 526} phosphoric,^{524, 526} or alkanesulfonic.⁴⁹² Ethylene combines with hydrogen sulfide under pressure in the presence of phosphoric acid on kieselguhr at 220 to 350°. ⁵⁵⁸ Hydrogen sulfide is added to aliphatic hydrocarbons having several olefinic bonds in the presence of acid phosphorus compounds at 50 to 100°. ³⁰ Secondary and tertiary mercaptans are formed with the aid of sulfuric.³⁷⁴ An acid or a basic catalyst may be used.^{82b} High yields of *t*-butyl and *t*-amyl mercaptans are obtained from isobutylene and isopentylene with hydrogen sulfide at moderate temperatures and pressures in the presence of acid catalysts,^{5, 546} or of a clay catalyst.⁵⁶⁰ Under mild conditions the reaction is selective; the product from a mixture of butene and isobutene is pure *t*-butyl mercaptan.²⁷ Pure *i*-butene can be obtained by cracking the *t*-butyl mercaptan so prepared.²⁸ *t*-Butyl and *t*-*i*-octyl mercaptans are now manufactured on a considerable scale. With abietyl compounds bases are more effective.^{82a} Basic catalysts are recommended for the addition of hydrogen sulfide to a variety of compounds, $\text{RCH}=\text{CH}_2$.³⁰⁶ 3-Hexene and anhydrous sodium hydrosulfide in alcoholic solution give hexanethiol-3.⁵⁷⁷ Molybdenum sulfide ^{160a} is recommended as a catalyst. Water-binding agents, such as acid anhydrides, are used with metal sulfides, such as those of nickel and iron ^{452a, 663, 664} at elevated temperatures and under pressure. Depolymerization and addition of hydrogen sulfide may go on simultaneously as when triisobutylene and hydro-

gen sulfide are heated at 100 to 300°, under 500 to 1500 lb. pressure with a claylike catalyst.⁵¹¹ Peroxides and strong acid salts of iron, chromium, magnesium, aluminum, thorium, uranium, cerium, lanthanum, beryllium, osmium, molybdenum, vanadium, and manganese are claimed as catalysts.^{452b} Friedel-Crafts catalysts,^{52, 458} aluminum chloride,^{53, 172, 458} boron trifluoride,^{53, 172, 173, 175b, 194, 458, 553a, 581} hydrofluoric acid,^{53, 172, 458} and stannic chloride^{175a, 425, 458, 581} are effective. Addition of hydrogen sulfide to ethylene, acrylonitrile, styrene, and other unsaturates takes place readily in alcohol containing sodium ethylate or ammonia.^{310, 333} Certain azo compounds are useful catalysts.⁴⁷⁸

Of all catalysts so far tried, 'ultraviolet light is by far the most effective. Butene-1 and liquid hydrogen sulfide, in a sealed tube exposed to the light from a mercury arc, showed 80% conversion in 4 minutes at 0°, 15% of this to butyl sulfide and 85% to *n*-butyl mercaptan. In 6 minutes under the same conditions propylene gave 65% *n*-propyl mercaptan and 35% sulfide. The -SH adds to the carbon having the most hydrogen contrary to Markownikow's rule. Acetone and lead tetraethyl are photosensitizers and increase the yield.^{188, 632, 633} Cyclohexene and 1-methylcyclohexene react similarly.⁴⁴² In the gas phase the reaction is slow.

Addition to unsaturated ketones takes place readily.⁴⁸⁷ Hydrogen sulfide is added to an α,β -unsaturated ketone.^{106, 667} The addition compound, $(C_{10}H_{14}O)_2H_2S$, is used for the isolation of carvone.²⁰⁸

Acetylene and hydrogen sulfide unite to give thioacetaldehyde, vinyl mercaptan, vinyl ethyl sulfide,³⁰⁸ and other products when these gases are brought together in a solvent with or without an alkaline catalyst.⁵¹⁰ At higher temperatures thiophene^{540, 596} and thiophenol⁶³ are formed.

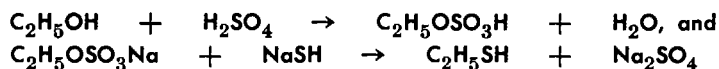
FROM ESTERS OF INORGANIC ACIDS

The first preparation of a mercaptan was by Zeise^{686a} in 1834. He saturated barium sulfide with hydrogen sulfide and heated it in a retort with calcium ethyl sulfate. Liebig^{387b} used the corresponding potassium compounds. A small yield of thiophenol was obtained by Stadler by fusing together solid sodium benzenesulfonate and solid potassium hydrosulfide.⁵⁸⁰

A frequently used method of preparing ethyl mercaptan is that

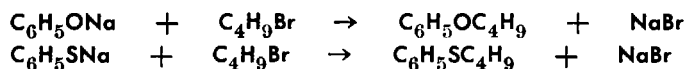
of Klason.^{344a, 344b} To a mixture of 500 cc. of concentrated and 500 cc. of fuming sulfuric acid, 1 liter of absolute alcohol is added. After this mixture has cooled, it is diluted by throwing in ice and poured into a cold aqueous solution of 4 kg. crystalline sodium carbonate. The faintly alkaline solution is concentrated by evaporation on a steam bath and cooled to eliminate most of the Glauber's salt. A solution of 800 g. of potassium hydroxide in 1600 cc. of water is saturated with hydrogen sulfide. The two solutions are mixed and heated on a steam bath. The liquid which goes over is freed from hydrogen sulfide with mercuric oxide and taken up in potassium hydroxide solution. The undissolved ethyl sulfide is separated and the mercaptan liberated with acid. A yield of 290 g. or 27% has been reported. The author prepared 1400 g. of ethyl mercaptan by this method in 1909 and found it satisfactory. Methyl,^{253, 344a, 344b, 453} *i*-butyl,²⁹⁹ and *i*-amyl³⁶¹ mercaptans have been prepared similarly. From 500 cc. of *n*-butanol the yield was 120 g. or 25%.⁴³⁵

These are over-all yields from the two reactions:



The first of these is an equilibrium reaction and a considerable amount of the alcohol is left over unless much fuming sulfuric acid is used. As the lower alcohols are plentiful, the low yield has been of little consequence. From solid potassium ethyl sulfate the yield is good.¹⁹⁵ By modern methods alcohols can be sulfated quite completely. Dodecyl^{182, 276a} and the higher alcohols from the methanol synthesis³⁹⁰ have been sulfated and used for making the corresponding mercaptans.

The fact that sodium alkyl sulfates are soluble in water, even when the alkyls are long carbon chains, is a great advantage but usually this is offset by their slowness to react. They are seldom employed for other alkylations, but when sulfur is involved they are satisfactory. Of the two reactions:



the second goes about a thousand times as fast as the first.⁴⁹⁶ In the preparation of mercaptans the inactivity of the sodium alkyl sulfates is compensated by the activity of the sulfur.

It is to be remembered that sodium hydrosulfide always contains some of the sulfide:



The sodium sulfide that is present reacts with the alkyl sulfate:

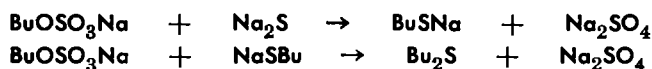


Thus there will always be some alkyl sulfide formed along with the mercaptan. The solubility of hydrogen sulfide in liquids decreases as the temperature is raised. If any of it is lost, the amount of sulfide is increased. It is desirable to counteract this by passing in hydrogen sulfide during the reaction or, better still, effecting the reaction in an autoclave under a high pressure of hydrogen sulfide. In this way the yield of mercaptan can be increased at the expense of the alkyl sulfide. Taking butyl sodium sulfate as an example, there is another reaction:



The higher the pH the more the alkene will be split off. An increase of the partial pressure of hydrogen sulfide lowers the pH and represses alkene formation. The tendency to form alkenes is small with the derivatives of primary alcohols but may be considerable with secondary and great with tertiary.

Some alkyl sulfide is obtained from sodium hydrosulfide. Conversely some mercaptan may be isolated even when pure sodium sulfide is the reactant. The reaction of sodium butyl sulfate with sodium sulfide must go in two steps:



The second reaction depends on the presence of the sodium mercaptide in the solution. This, being the salt of a very weak acid, is highly dissociated:

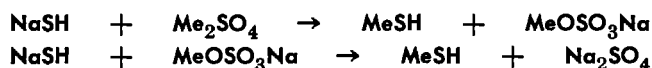


As will be explained more fully in a later chapter, butyl mercaptan is easily removed from water, even in the presence of a high concentration of sodium hydroxide, by steam distillation. In a recorded experiment²⁵¹ in which a solution of butyl sodium sulfate and sodium sulfide was boiled gently and the vapors allowed to pass out through a condenser, 31% of the butyl groups

formed in the distillate were in the mercaptan and 69% in the sulfide. If the butyl mercaptan had not been allowed to escape, practically all of it would have gone to make butyl sulfide. The preparation of ethyl mercaptan goes well since it is so volatile that most of it escapes before it can be converted to ethyl sulfide.

If, in the above experiment, a vigorous current of steam had been passed in to carry over the mercaptan as fast as it was formed, the yield of mercaptan should have been even higher. This suggests that, in the usual preparation of mercaptans from sodium hydrosulfide, the proportion of mercaptan to alkyl sulfide can be raised by blowing in steam during the reaction to carry off the mercaptan as it is formed. This should be of service from propyl to *n*-nonyl. *n*-Nonyl mercaptan boils at 220.2° and has a vapor pressure of about 15 mm. at 100°. It should go over with about six times its weight of steam. If an autoclave is used, the addition of a hydrocarbon to the mixture should be beneficial. A large proportion of the mercaptan should pass into the hydrocarbon layer and escape further reaction. For convenience of fractionation, a hydrocarbon should be selected that boils considerably above or below the mercaptan.

Dimethyl and diethyl sulfates, which have become commercially available in recent years, are the most convenient reagents for making methyl and ethyl mercaptans. They react in two stages:



The first stage is extremely rapid. The second goes well enough. Methyl and ethyl chlorides and bromides are inconveniently volatile and the iodides are expensive. The dialkyl sulfates are relatively nonvolatile and cheap and react well in aqueous solution.^{147, 341, 656}

When hydrogen sulfide is passed into a solution of ethyl nitrite in alcoholic ammonia, the mercaptan is formed.³⁵⁶ The esters of *p*-toluene sulfonic acid are readily prepared and are active alkylating agents. They have been used for making mercaptans^{557, 683} and are particularly suitable for preparing optically active mercaptans.³³¹

When ethyl alcohol and sulfur dioxide are heated in a sealed tube to 200°, disproportionation takes place and a number of compounds are formed: $\text{C}_2\text{H}_5\text{SH}$, $(\text{C}_2\text{H}_5)_2\text{O}$, $\text{C}_2\text{H}_5\text{SO}_3\text{H}$,

$C_2H_5OSO_3H$ and sulfur.^{186, 463} When *i*-amyl alcohol and an equal amount of sulfuric acid are heated to 170°, some mercaptan is produced along with amylene and its polymers.⁴⁹⁸

FROM ALKYL HALIDES AND METAL SULFHYDRATES

As alkyl halides are readily available in organic laboratories, they have been the usual starting compounds for preparing mercaptans. Regnault⁵⁰⁵ in 1840 passed ethyl chloride into potassium hydrosulfide in a tubulated retort and got the mercaptan. In the same year Löwig and Weidmann³⁹³ made ethylene mercaptan from ethylene chloride. Mercaptans were prepared from amyl chloride,³² cetyl chloride,²²¹ allyl iodide,²⁸⁸ hexyl chloride,⁴⁷² β -hexyl iodide,^{187, 650} *i*-propyl iodide,^{128a, 277} *s*-butyl iodide,⁵¹³ *n*-butyl iodide,²⁴⁹ melissyl chloride,⁴⁷⁷ heptyl chloride,^{668a, 668b} propyl bromide,^{519, 668a, 668b} octyl chloride,³²⁴ and *s*-heptyl iodide.^{278d, 279} Mercaptans up to octadecyl have been prepared from alkyl iodides and bromides,^{135, 206, 437, 512, 531} Optically active mercaptans have been obtained from the corresponding alkyl halides.^{215, 270, 380a, 380b, 390d, 380g} The addition of a small amount of a strong reducing agent to the reaction mixture is said to improve the yield of mercaptan.⁶⁶⁹ Tetrahydrofurfuryl alcohol is said to be a suitable medium for reactions of this sort.⁵³⁷

As a lecture demonstration, a 3-g. piece of potassium hydroxide is dissolved in 20 cc. of alcohol and saturated with hydrogen sulfide. Ethyl chloride is squirted in and the flask corked. Potassium chloride begins to precipitate. After an hour water is added and the mercaptan separates.²³⁶

Bromocellobiose has been converted to the mercaptan.⁶⁷⁵ Cyclopentyl bromide gives a fair yield of cyclopentyl mercaptan and little cyclopentene,³⁹¹ while cyclohexyl bromide gives little cyclohexyl mercaptan and much cyclohexene.^{82a}

The reaction rates of various bromides with potassium hydrosulfide and sulfide have been measured. Some hydrobromic acid is always split off, leaving some alkene.³⁹¹ The mechanism of the reaction has been studied.⁴⁵⁴

t-Butyl iodide and zinc sulfide give *t*-butyl mercaptan.¹⁶² A peculiar method of preparing mercaptans is the addition of bromine to a mixture of an alcohol, phosphorus, and sodium sulfate. Phosphorus tribromide is formed and reacts with the alcohol to produce an alkyl bromide. The phosphorous acid reduces the sulfate to sulfide and the mercaptan results.⁴¹⁹

Polyhalogenated higher hydrocarbons^{154, 215, 305, 311, 330} and halogenated terpenes⁴⁶⁰ may be the starting compounds in the preparation of mercaptans. Unsaturated halides, except those in which the halogen is attached to a doubly bound carbon atom, react satisfactorily.^{112, 157, 255, 375a}

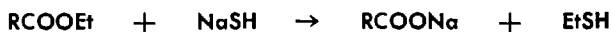
The action of sulfur monochloride on anthracene introduces the -SSCl group in the 9-position. Treatment of this with sodium sulfide gives 9-anthracenethiol.^{224, 475} Similar reactions take place with 1,2-benzanthracene and with 3,4-benzpyrene.⁶⁷³

An aromatic halide, such as phenyl chloride or bromide, does not react with an alkali hydrosulfide under mild conditions, unless the halogen is activated by a group, such as the nitro, in the ortho²⁸⁶ or para position. 4-Nitrochlorobenzene⁵⁷² and 1,4-nitrochloronaphthalene³⁹⁶ react satisfactorily to form the mercaptans. When two nitro groups are in certain relative positions, one of them is activated.²⁸⁵ A halogen in the side chain,^{370, 574} as in benzyl chloride, is reactive. Benzyl mercaptan is obtained from it readily.^{14, 394, 457, 592} Under pressure and above 300°, phenyl chloride does react with sodium sulfide to give a mixture of thiophenol, phenyl sulfide, and phenol.⁶⁴² Other aromatic halides react under similar conditions.

Alkyl halides and hydrogen sulfide react even in the absence of alkali. Some mercaptan is formed when an aqueous solution of methyl iodide is saturated with hydrogen sulfide.¹⁰² Tertiary alkyl halides react with hydrogen sulfide in the presence of a Friedel-Crafts catalyst, such as stannic chloride.^{175b} Hydrogen sulfide, passed into a solution of triphenylmethyl chloride, in which activated alumina is suspended, gives triphenylmethyl mercaptan.³³⁵

Chlorinated aromatics, such as chlorobenzene and *p*-chlorotoluene, passed in vapor form over catalysts at elevated temperatures, 400 to 700°, with hydrogen sulfide, are converted to the corresponding mercaptans.^{122, 144, 265}

An ester may function as an alkyl halide:



This is effected at 180° with all reactants dry. Ethyl formate, valerate, and succinate and *i*-amyl acetate and butyrate have been studied.¹³ Esters of *p*-toluenesulfonic acid are particularly useful.¹⁶⁴

When hydrogen sulfide is passed into a solution of aluminum bromide in ethyl bromide a complex, $\text{AlBr}_3 \cdot \text{H}_2\text{S} \cdot \text{EtBr}$, is formed. This is hydrolyzed by water into hydrobromic acid, aluminum bromide, and mercaptan.⁴⁸¹

Since the alkyl halides, except the very low ones, are practically insoluble in water, it is necessary to use alcohol as a solvent. As a starting material potassium hydroxide is preferable to the sodium compound since it is more soluble in alcohol. When an alcoholic solution of sodium hydroxide is being saturated with hydrogen sulfide, the intermediate sodium sulfide, which is only slightly soluble in strong alcohol, may separate out and give trouble. The equilibrium between sodium hydrosulfide and sodium sulfide plus hydrogen sulfide shifts to the right when the temperature is raised since hydrogen sulfide is less soluble. Therefore, more of the mercaptan and less of the by-product alkyl sulfide is formed when the reaction is conducted at room temperature. For 1 mole of an alkyl halide, dissolve 54 g. sodium methylate, or 23 g. sodium, in 300 cc. of alcohol. Add the alkyl halide, shake to mix and let it stand until the precipitation of the sodium halide appears to be complete. Filter off the salt and fractionate the alcohol solution. On account of the formation of azeotropes of the lower mercaptans with alcohol, this method should not be used for mercaptans below hexyl.^{506b} The lower alkyl chlorides, up to amyl, react satisfactorily with aqueous sodium hydrosulfide and the mercaptans can be steam distilled from the reaction mixture.¹²⁷

For alkyl halides up to *n*-nonyl,^{184, 375a, 375b} 400 to 500 cc. of alcohol is used per mole. Above amyl this should be absolute alcohol. In a particular preparation, 90 g. of potassium hydroxide was dissolved in the alcohol and saturated with hydrogen sulfide which was passed in all during the reaction. The alkyl halide was added dropwise and the mixture kept at room temperature for several hours and then heated to reflux for an hour. For *s*-octyl and *s*-nonyl it was found best to dissolve 40 g. sodium in 500 cc. of absolute alcohol and saturate this with hydrogen sulfide.^{525, 693} The addition of water to the reaction mixture causes the mercaptan to separate. This serves well for the preparation of triphenylmethyl mercaptan.⁶⁴¹ For high molecular weight mercaptans, such as cetyl,¹³⁵ heating the reactants in an autoclave is desirable. Butanol containing some water is recommended as a

solvent for reactions involving alkyl chlorides, decyl to octadecyl.⁴⁷

It is impossible to direct the reaction so that only mercaptan is formed.^{38, 375a, 375b} When the alkylating agent is a nonvolatile, water-soluble alkyl sodium sulfate, it is possible to distil out the mercaptan as it is formed and thereby diminish the opportunity for the formation of alkyl sulfide. When it is an alkyl halide, this cannot be done since the volatility of a mercaptan is less than that of the corresponding alkyl chloride and about equal to that of the bromide. It may be possible to arrange a continuous process so that this difficulty can be overcome. If an alkyl halide, such as ethyl chloride, is forced in at the bottom of a heated column of sodium sulfhydrate solution, it will be changed into mercaptan as it goes up. If the column is tall enough, the transformation should be complete. As the reaction is a rapid one, the required height of the column may be within the limit of practicability. The application of pressure would raise the working temperature and permit the use of a shorter column. A high boiling halide, such as lauryl chloride, might be mixed with a hydrocarbon, such as xylene. The xylene solution of the mercaptan would collect at the top of the column and be drawn off.

It has been customary to separate the mercaptan from the alkyl sulfide by-product by dissolving it in aqueous caustic soda solution, drawing off the undissolved sulfide and freeing the mercaptan by adding acid. As will be explained in Chapter 2, this method is practicable for only the lower mercaptans since the higher ones are easily extracted from 10% aqueous alkali. When a higher mercaptan has to be dealt with, 10 to 30% of alcohol must be added to the alkaline solution. This has little effect on the solubility of the sulfide, but a great effect on that of the mercaptan.

Besides being inefficient, this method of separation is objectionable since the oxygen of the air forms disulfides rapidly in the presence of alkali.⁴⁷⁸ This has been overlooked by many chemists, though the presence of disulfide has been noted.⁴³⁷ To avoid this an alkaline solution of a mercaptan should be kept out of contact with air as far as possible. When such a solution is to be acidified, it should be run into the acid. Pouring acid into alkali generates heat and accelerates the oxidation of the mercaptan while the solution is still alkaline.

With modern stills the separation of a mercaptan from concomitant sulfide and disulfide by fractionation presents no difficulty. The boiling points of several mercaptans and the corresponding chlorides, bromides, and sulfides are given in Table 1.1.

TABLE 1.1

Boiling Points of Mercaptans, Chlorides, Bromides, and Sulfides

Alkyl	Mer- captan	Chloride	Differ- ence	Bromide	Differ- ence	Sulfide	Differ- ence
Methyl	6.0°	-23.7°	29.7°	3.6°	-2.4°	37.3°	31.3°
Ethyl	34.7	12.2	22.5	38.4	3.7	92.2	57.5
Propyl	67.5	46.6	20.9	71.0	3.5	142.0	74.5
Butyl	98.0	78.5	19.5	101.6	3.6	182.0	84.0
Amyl	126.5	108.3	18.2	129.7	3.2	230.1	103.6

The boiling points of the mercaptans and of the corresponding bromides are inconveniently close. For this reason care should be taken to cause the bromides to react completely.

BY HYDROLYSIS OF A THIOESTER

Thioacetates

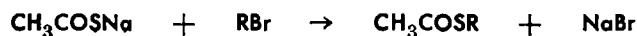
The hydrolysis of a thioester gives a mercaptan: ^{506a}



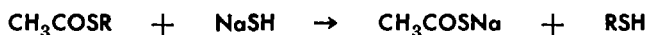
Thiolesters are readily hydrolyzed and the mercaptan produced can contain no alkyl sulfide or halide. Esters of thioacetic acid are particularly suitable.^{568a} Glucothiose has been made in this way.^{536, 551} It is preferable to use ammonia instead of alkali in decomposing the thioacetate. Ammonia reacts rapidly with thioacetic esters:



There is less danger of oxidation when strong alkali is avoided. The thioacetic esters can be obtained by the reaction of an alkyl halide or sulfate on sodium thioacetate:



This reaction goes readily and gives high yields since the sodium is joined to sulfur. As there is only one sodium on the sulfur there is no possibility of the formation of an alkyl sulfide or other troublesome by-product. If the thioester is saponified with sodium hydrosulfide, sodium thioacetate is regenerated and may be used for making more of the ester:

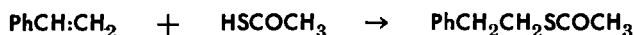


The neatest way to recover the mercaptan from the thioester is by methanolysis. The thiol ester is dissolved in 2 or 3 volumes of absolute methanol to which about 0.2% of sodium has been added. The mixture is warmed. Transesterification takes place immediately:



As the methyl acetate boils at 57.2°, it is easily driven off. Taking off the excess methanol leaves the mercaptan which may be distilled without purification. As the separations are to be made by fractionation, the boiling point of the mercaptan must be considered, which for ease of fractionation should be above 100°. Higher-boiling mercaptans should be distilled at appropriately reduced pressures. If the starting material is a pure thiolester the yield is quantitative except for losses in handling.

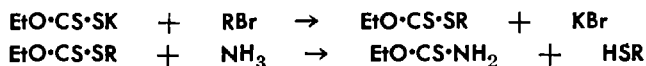
The preparation of mercaptans by the hydrolysis of thioacetic esters is likely to become of great importance since many of these esters are formed by the direct addition of thioacetic acid to unsaturates. (See the chapter on thioacids.) As the addition of thioacetic acid takes place contrary to Markownikow's rule, an alpha-olefin is converted into a primary mercaptan which might not be the case if hydrogen sulfide were added to the same olefin. Styrene and thioacetic acid unite:



Hydrolysis of this yields phenylethyl mercaptan, $\text{PhCH}_2\text{CH}_2\text{SH}$.
103, 289b

Thiocarbonates and Thiocarbamates

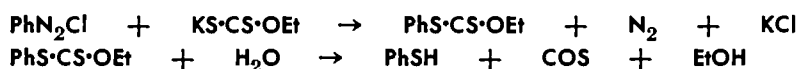
The xanthates are readily available and are good starting materials for preparing thioesters which can be made to yield mercaptans:



This method is particularly convenient for water-soluble halides, such as chloroacetic acid: 65, 222, 289a

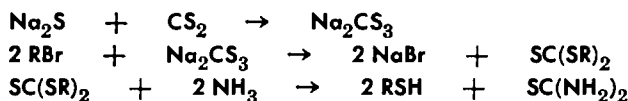


It has long been a standard method for making aromatic mercaptans. It is particularly useful for that group since aromatic halides are relatively unreactive and since diazonium compounds are readily available. A diazonium salt reacts with a xanthate: 163, 268, 377, 598



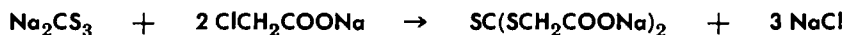
As the alcohol involved in making the xanthate does not influence the mercaptan, a cheap alcohol, such as ethyl, is used. It might be desirable to use one such as *n*-butyl which is easily recovered. The inconvenience of handling hydrogen sulfide is avoided by the xanthate method. One half of the sulfur in the carbon disulfide is used. *m*-Nitrothiophenol has been made by this method.^{79, 378}

Sodium trithiocarbonate, Na_2CS_3 , has possibilities that have not been fully realized:



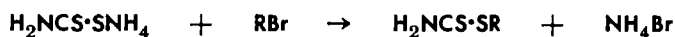
Carbon disulfide is added dropwise to a 1 molar solution of sodium sulfide (240 g. $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ made up to 1 liter), containing magnesium hydroxide (10 g. $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ and 4 g. NaOH dissolved in water and added separately).⁴⁶⁷ This solution should be well stirred and kept at about 50° during the addition. When the carbon disulfide has all reacted, the temperature is raised to 70° and the alkyl halide added dropwise, continuing the stirring.

This method is particularly suitable for alkyl sulfates or water-soluble halides, such as chloroacetic acid:



The trithiocarbonic ester is hydrolyzed to get the mercaptan.

Ammonium dithiocarbamate, from the union of carbon disulfide and ammonia, reacts well with an alkyl halide:



Hydrolysis, or pyrolysis, of this ester gives the mercaptan.^{91a, 91b, 92, 93}

One of the products of the reaction of phosphorus pentasulfide on an alkene is a thiophosphoric ester from which a mercaptan is obtained by hydrolysis.²⁹⁸

Bunte Salts

The cheapest and most available salt of a thioacid is sodium thiosulfate. It reacts with an alkyl halide:

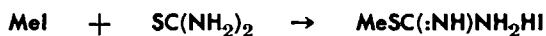


The alkyl thiosulfate is a so-called Bunte salt. It can be hydrolyzed and the mercaptan set free.^{105, 281, 490a, 518, 591} This method has seldom been used for preparing mercaptans, but is convenient when their derivatives, such as disulfides or mercaptals, are desired, since these can be obtained directly from the Bunte salts. For making mercaptans the drawbacks are that the formation of the Bunte salt is slow and its hydrolysis is not clean cut. *m*-Nitrothiophenol has been made by treating the Bunte salt with concentrated hydrochloric acid.³⁷²

From Thiourea

In recent years the thiourea method has practically superseded all others for the preparation of mercaptans on the laboratory scale. It is easy to operate and has the advantage that no alkyl sulfide is formed as a by-product. A wide variety of halides may be used.^{21, 200, 214, 282, 339a, 339b, 385, 520, 599} It works well with many dihalides.²⁵⁴

It was observed by Claus in 1875 that ethyl bromide and thiourea unite to form a crystalline salt which is decomposed by alkali. A similar salt was obtained with chloroacetic acid.^{128b} Two years later Willgerodt heated two molecules of dinitrochlorobenzene with one of thiourea in 90% alcohol in a sealed tube at 100 to 155°. He isolated dinitrophenyl mercaptan, ethyl chloride, ammonia and carbon dioxide.^{661c} Methyl iodide and thiourea react on standing, even in the cold:

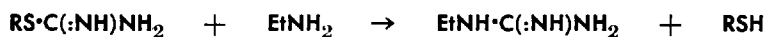


The salt, S-methylisothiuronium iodide, is stable and soluble in water. When methyl iodide is added to powdered thiourea moistened with ethanol the reaction is so vigorous that a reflux condenser is needed.⁶⁵⁸ The same is true of ethyl iodide.⁶⁵⁷ The ad-

dition of aqueous alkali, or ammonia, causes the separation of the free base, $\text{MeSC}(:\text{NH})\text{NH}_2$, which is only slightly soluble in water. Warming the base with water causes it to split into the mercaptan and cyanamide: ⁵⁸



This reaction is reversible. The cyanamide polymerizes to di-cyandiamide but this is of no consequence as far as the preparation of the mercaptan is concerned. Decomposition may be effected by an amine: ⁵³⁵



The by-product is a substituted guanidine. As substituted thioureas may be used as starting materials, this makes possible the synthesis of a wide variety of substituted guanidines.

The thiourea method has given good results with a tertiary halide,²⁰ with unsaturated chlorides, such as methallyl²² and crotyl,⁹⁵ with chlorhydrins,⁴⁵⁶ and with substituted benzhydryl halides.²²⁹ Dehydroisoandrosteryl mercaptan⁵⁷ and 9,10-anthracenedi(methanethiol) have been prepared by this method.⁶⁰⁷ The yield of cyclohexyl mercaptan is satisfactory,⁵⁸² whereas the yield of this mercaptan by the sodium hydrosulfide method is poor.

The operations are conveniently carried out in a three-necked flask which is provided with a dropping funnel, a steam inlet tube, and a condenser, set for reflux. The thiourea is placed in the flask with about two thirds its weight of water. For mercaptans up to decyl, the use of alcohol is not only unnecessary but is objectionable, on account of the formation of azeotropes of the lower mercaptans with alcohol and the low solubility of thiourea in alcohol.^{506b} For higher alkyl halides, one fourth to one half of the water may be replaced with alcohol. (Alcohol of 95 ⁶³⁰ or 99% concentration has been used as solvent with cetyl bromide,⁶² but 50% alcohol is a better solvent for the thiourea and dissolves sufficient amounts of even the higher alkyl bromides to keep the reaction going.^{506b}) Heat is applied and the halide is added dropwise or in portions. The reaction may be over in 15 minutes or may require several hours. When the combination is judged to be complete, the condenser is turned down and steam passed through to remove alcohol or other volatile matter. The receiver is changed and concentrated sodium hydroxide solution added

from the funnel at such a rate that the reaction is vigorous but can be kept under control. A volatile mercaptan, up to octyl or nonyl, goes over and is separated from the water layer of the distillate. The water layer can be discarded. Ether extraction is useless since 1 liter of water dissolves only 0.57 g. of butyl mercaptan and much less of the higher. When the mercaptan is fractionated, the first portion that goes over is turbid and carries all of the water that is present. Only this tiny portion need be dried. Except for mechanical losses, the yields are practically theoretical. For nonvolatile mercaptans steam is used only for getting rid of volatile materials. Precautions must be taken to minimize the oxidation of the mercaptan by air, which is rapid in the presence of alkali. Air may be displaced by nitrogen or by adding a little benzene which will provide a blanket of vapor. Just as soon as the liberation of the mercaptan is complete, sufficient acid is added to bring the pH below 7. The reaction mixture is cooled and the mercaptan layer taken off.⁵⁰⁷

For methyl mercaptan it is convenient to prepare a quantity of the crystalline methylisothiuronium salt which can be stored and used as desired. One mole of thiourea (76 g.), 50 cc. of water and 63 g. (0.5 mole) dimethyl sulfate are warmed together in a flask until all go into solution. The solution is boiled vigorously, without reflux. Crystals begin to separate in 5 to 10 minutes. The boiling is continued until a thick magma is produced. The formation of a fog is to be avoided. A little cold water and sufficient alcohol to double the volume are added and the mixture cooled and filtered. The yield is 105 g. of the salt. By boiling down the mother liquor and adding alcohol, 20 g. more can be obtained, which corresponds to a yield of 90%. This salt melts at 244° with decomposition. To generate methyl mercaptan, 70 g. of this salt and 100 cc. of 20% sodium hydroxide solution are heated gently in a flask with a reflux condenser. Methyl mercaptan is evolved regularly. It passes up through the condenser, is bubbled through dilute sulfuric acid, and dried with calcium chloride. The yield is 21 to 22 g. or 90% and the operation requires only 10 to 25 minutes.^{9, 23, 556, 666}

The thiourea method is especially advantageous when the mercaptan is being made as an intermediate for the preparation of some derivative, such as a mixed sulfide. Thus, in the described preparation, as soon as the isothiuronium salt has been prepared

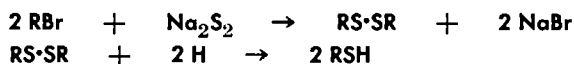
and volatile materials have been removed by steam distillation, the condenser is turned to reflux and twice the usual amount of alkali is added together with the other alkyl halide. As the mercaptan is liberated, it forms sodium mercaptide which reacts at once with the alkyl halide.³⁰¹ For example, add one mole of hexyl bromide to a slight excess of thiourea in twice its weight of water and reflux until the reaction appears to be complete. Add to the hot mixture slightly more than a mole of concentrated aqueous sodium hydroxide. When the mercaptan separates as a layer, add one mole of butyl bromide and another of the alkali. A volatile sulfide can be driven over with steam, while a less volatile may be separated from the cooled mixture.^{506b} The mixed sulfide $S(CH_2CH_2SCH_2CH_2OH)_2$ was prepared by the addition of ethylene chlorhydrin. The elapsed time from the start of the heating to the pouring out of the product was 90 minutes.⁵⁰⁴

The preparation of the alkyl halide and its utilization to form the S-alkylisothiuronium salt may be accomplished in the same flask. A solution of thiourea in 10 parts of ethanol containing hydrogen chloride, refluxed several days, gave the desired salt.⁵⁸⁸ A mixture of 75 cc. of ethanol containing 4.5 g. hydrogen chloride and 7.6 g. thiourea was refluxed 72 hours to give 30% ethanethiol or 120 hours for 61%.^{321, 579} By the use of hydrobromic acid, the reaction time can be shortened greatly.²¹³ It might be assumed that ethyl chloride is formed which subsequently reacts with the thiourea in the usual way. Against this it may be said that it does not seem likely that ethyl chloride, which boils at 12.2° , would remain in boiling alcohol long enough to react with anything. Alkyl chlorides do not react rapidly with thiourea. Perhaps the alcohol reacts in some way with the thiourea hydrochloride or with the thiuronium ion. This method is not recommended except in special cases, such as with alcohols whose hydroxyls are labile. The best example is thiodiglycol. One mole of thiodiglycol (122 g.), 2.02 moles of thiourea (155 g.), and 200 cc. of concentrated hydrochloric acid are heated under reflux. The formation of the thiuronium salt is complete within 20 minutes. The mercaptan, $S(CH_2CH_2SH)_2$, is liberated with alkali in the usual way. A yield of 85% of the distilled mercaptan has been obtained, the same as from mustard gas. In this case there is the special advantage of not having to handle the toxic chloride.⁵⁰⁴

BY REDUCTION

Disulfides

Alkyl disulfides are obtained from reactions with sodium disulfide and can be reduced to the mercaptans:⁴⁵⁰



The reduction may be effected in various ways.^{126, 181, 276b, 317, 319, 468, 501, 541, 578, 621, 692} Alkyl and aryl disulfides and many other sulfur compounds are reduced neatly by lithium aluminum hydride to the mercaptans.^{11, 593, 594} Hydroxymercaptans are advantageously prepared by way of the disulfides.^{227, 568b, 569} This method is particularly suitable when the disulfide can be prepared by some special method, as is the case with furfuryl disulfide.^{243, 313, 340, 376, 584}

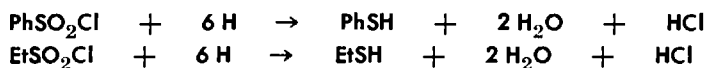
This would look like a way of circumventing the formation of the alkyl sulfide along with the mercaptan. Unfortunately sodium disulfide is a "statistical" compound, an equilibrium mixture of the disulfide with monosulfide and polysulfides:



The amount of alkyl monosulfide formed will depend on the proportion of sodium monosulfide present and on the relative reaction rates of it and of the di- and trisulfides with the alkylating agent. Experiments have shown that some alkyl monosulfide is produced even when the composition of the sodium polysulfide corresponds to Na_2S_4 . To cut down the formation of the monosulfide, it is desirable to use sodium tri- or tetrasulfide. The alkyl polysulfides are readily reduced to the disulfides and to the mercaptans. Catalytic hydrogenation with a metal sulfide catalyst is applicable.^{190b} The separation of the mercaptan from sulfide and disulfide by fractionation is a simple matter. *m*-Nitrothiophenol has been made by reducing the disulfide with glucose⁵⁵ or sodium sulfide,⁸⁸ both in alkaline solution.

Other Reductions

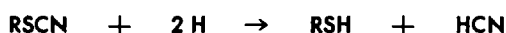
A sulfone chloride can be reduced to a mercaptan by zinc and an acid: 29, 35, 83a, 85, 176, 223, 235, 256, 267, 345, 348, 484, 623, 665, 688, 691



Tin or stannous chloride may be used.^{231, 296, 585, 622} *p*-Phenylene dimercaptan⁶⁸⁹ and 4,4'-dimercaptodiphenyl^{411b} have been made by the reduction of the respective disulfone chlorides with zinc and acid. This has been a standard method for making aromatic mercaptans, but has been seldom used for aliphatic mercaptans⁶³⁹ since the required sulfone chlorides are not so readily available. Catalytic hydrogenation has been recommended for aliphatic sulfone chlorides.^{211a, 628} Lithium aluminum hydride^{198, 411a} and phosphorus with potassium iodide³⁴³ have been used as reducing agents.

An arylsulfinic acid or its salts may be reduced to a mercaptan with zinc and hydrochloric acid.^{133, 170a, 233, 275, 461, 462} 2-Thiophenesulfinic acid has been so reduced.⁶⁴ An arylsulfonamide is reduced by hydriodic acid.^{203, 204}

The reduction of cholesteryl thiocyanate by the Clemmensen method gives cholesteryl mercaptan: m. 99.5°, $[\alpha]_D - 23.85^\circ$.⁶⁴⁵ Hydrogenation of an alkyl thiocyanate gives a mercaptan:

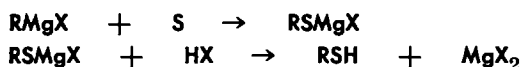


This does not seem to have been used as a preparation method.²³⁷

A selenocyanate is reduced by a metal and acid to the seleno-mercaptan.⁵⁸⁹

BY THE GRIGNARD REACTION

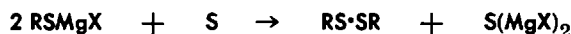
Sulfur reacts with Grignard reagents: 433, 603a, 603b, 603c, 603d



Selenium reacts similarly:



The examples given are aromatic, but aliphatic mercaptans can also be obtained in this way.^{209, 677} The yield may be as high as 80% provided there is no excess of sulfur:⁶⁷⁶



Cyclohexyl mercaptan, which is difficult to obtain by the usual methods, has been prepared by this method.^{83b, 405, 619} Most aliphatic mercaptans are so readily prepared by other methods that there has been little incentive to use this method except for *t*-butyl.⁵¹⁵ Thioborneol has been prepared by this reaction,^{269, 293} so have the two thiophenethiols.¹⁰⁷

Phenyllithium and sulfur give thiophenol.²⁴² Butyl mercaptan has been made from butyllithium.⁸⁰

CATALYTIC FORMATION OF MERCAPTANS

When coal gas is passed over heated powdered nickel, an organic sulfur compound is formed which gives a mercury derivative, m. 65 to 70°. ⁴³⁰ Sabatier and Mailhe passed primary and secondary alcohols with hydrogen sulfide over heated thoria which they found to be the only efficient catalyst. ^{528a, 528b} They report yields of 50 to 75%. Secondary alcohols of five to nine carbon atoms gave mercaptans. ^{404a} A later study gave the following yields for 1:1 mixtures of alcohol vapor and hydrogen sulfide over thoria at 380°: methyl 42%, ethyl 35%, propyl 45%, *n*-butyl 52%, *i*-butyl 36%, and *i*-amyl 42%. ³⁵⁹ It was found that the mode of preparation of the thoria is of great importance. The catalytic preparation of mercaptans up to octadecyl by passing their vapors and hydrogen sulfide over a dehydrating catalyst, such as zirconia, has been claimed. ^{41, 307} The presence of a small amount of hydrogen in the mixture of methanol vapor and hydrogen sulfide is said to cut down the formation of methyl sulfide. ⁵² The catalytic preparation of the higher mercaptans is now in commercial operation.

An alcohol may be heated with sulfur and hydrogen, under pressure with a catalyst, to produce a mercaptan. The yield from laurol is 40%. ⁵⁹⁸ Cyclohexyl methyl mercaptan has been made by passing the acetate with hydrogen sulfide and hydrogen over a cobalt sulfide catalyst. ⁴⁷⁰ Phenols are converted to thiophenols by passing their vapors over alumina, or thoria, with excess hydrogen sulfide at 400° to 600°. ³⁴ Passing alcohol and carbon disulfide vapors over catalysts at 400° gives a moderate yield of mercaptan. The active agent may be the hydrogen sulfide formed by the action of the carbon disulfide on the water from the dehydration of a part of the alcohol. ²⁴⁰

Hydrogenation of carbon disulfide to methyl mercaptan in the presence of nickel polysulfide approaches a first-order reaction. ¹⁴¹ Hydrogenation of a nitrile in the presence of hydrogen sulfide with cobalt polysulfide catalyst gives the mercaptan. ^{170b, 505a} A carboxylic acid, or an ester, reacts with hydrogen sulfide in the presence of a hydrogenation catalyst to form a mercaptan. ^{180a, 180b, 602}

Mercaptans are produced by the hydrogenation over a sulfactive catalyst of a variety of sulfur compounds.^{170c, 171, 190a, 190b, 211b, 367, 368, 369, 565b, 605} A mercaptan results when an olefin, sulfur, or hydrogen sulfide, and hydrogen are heated with a sulfactive catalyst.^{4, 655}

t-Butyl sulfide can be cleaved to *t*-butyl mercaptan by hydrogen sulfide in the presence of metal sulfides.³ A sulfide may be cleaved by sodium in liquid ammonia.¹⁵⁸

During World War I, it was proposed to use *n*-butyl mercaptan as a camouflage gas to the end that the enemy would have difficulty in telling in which sectors toxic gases were being used and in which they were absent. A small plant rated at 300 lb. per day was set up at the American University in Washington for making *n*-butyl mercaptan catalytically. The alcohol vapors and hydrogen sulfide were passed through enamel-lined steel tubes 10 ft. long and 2 in. in diameter heated to about 400° C. The plant operated successfully and about a ton of the mercaptan was sent to France, but whether or not it was ever used, no one seems to know. The condensate from the catalyst tubes separated into two layers. The top layer was taken off and fractionated. The chief difficulty encountered was due to the fact that *n*-butyl mercaptan and *n*-butanol form an azeotropic mixture containing 14.84% of the alcohol and boiling at 97.8°.³⁵⁹

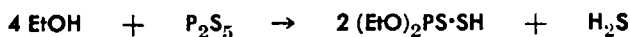
A method which is not catalytic but which uses the same operating conditions is to pass the alcohol vapor over aluminum sulfide. Much mercaptan and some sulfide are obtained at 260 to 300°.^{383, 384}

MISCELLANEOUS FORMATIONS

This is emphatically not a method for preparing mercaptans but is mentioned here since it has been taken up in many text books. Kekulé³²⁹ wrote the equation:



This cannot be realized under any conditions. The alcohol adds to the pentasulfide somewhat as it would to phosphorus pentoxide. According to conditions various products are formed. One important reaction is:⁴⁸⁰



Since the alkyl in this is still bound to oxygen, a mercaptan cannot be produced by simple hydrolysis but may be among the products of pyrolysis. This will come up again in Chapter 3. Thiophenol⁴⁹ and 2-hexyl-*p*-thiocresol²⁹² have been obtained from the hydroxyl compounds with phosphorus pentasulfide. Heating ethyl diphenylacetate with phosphorus pentasulfide gives ethyl mercaptan.⁵⁸³

Methyl mercaptan is formed from carbon disulfide and hydrogen sulfide in the presence of a Friedel-Crafts catalyst.⁵²

Cyclohexyl mercaptan is formed when cyclohexanone is heated with ammonium polysulfide.⁶⁸¹

Aromatic mercaptans are formed when sulfur chloride reacts with the hydrocarbon in the presence of aluminum amalgam.¹³²

Mercaptans seem to be among the products when an alkene and hydrogen are led over pyrites at 350° or when an alkene is treated with a sulfurizing agent, such as sodium tetrasulfide.³⁰⁹ Two mercaptans and other compounds result when 2-methylbutene-2 is heated with sulfur at 160 to 170°.¹⁰¹

Cyclohexane is sulfurized and dehydrogenated by sulfur to thiophenol.²²⁵ Mercaptans are commonly among the products when hydrocarbons are heated with sulfur. Propylene and sulfur give some *i*-propyl mercaptan.³⁹⁵

Thianaphthene is reduced by sodium in boiling alcohol to *o*-ethylthiophenol.²²⁰ By the same treatment, thienol [3,2-*b*]-thiophene is opened up to 2-ethyl-thiophenethiol-3.¹¹⁶

Triphenylcarbinol is converted to the mercaptan by saturating its solution in acetic acid with hydrogen sulfide in the presence of a catalytic amount of sulfuric acid.³³

Treating an epoxy resin with hydrogen sulfide is said to introduce sulphydryl groups.⁵⁵⁹

A by-product of the synthesis of thiophene from a succinic ester and phosphorus pentasulfide is 2-thiophene-thiol.⁴²³ The 3-isomer is a by-product in the commercial synthesis of thiophene from butane and sulfur.⁵⁰⁰

A silicon mercaptan, Me_3SiSH , has been prepared from the corresponding chloride by conventional methods.¹¹⁹

Dimercaptans or Dithioglycols

Derivatives of the *gem*-dithiols, $\text{RCH}(\text{SR}')_2$ and $\text{R}_2\text{C}(\text{SR}')_2$, the mercaptals and mercaptoles have been known for a long time.

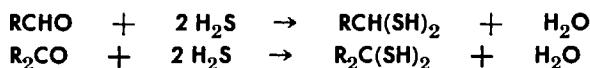
They are so numerous and so important that a whole chapter will be devoted to them. Until recently it was assumed that the *gem*-dithiols would be too unstable to be isolated. Chemists contented themselves with assuming their existence as intermediates.

By treating formaldehyde with hydrogen sulfide at low temperature, a liquid is obtained which is stable for a time if kept cold. Iodine converts it to a tarry mass from which a solid melt-

ing at 83 to 84° can be extracted, apparently $\text{CH}_2 \begin{array}{l} \diagup \text{SCH}_2\text{S} \\ \diagdown \text{SCH}_2\text{S} \end{array}$, m.wt.

calc. 170, found 165 to 177. By treating the original reaction product with methyl iodide in alkaline solution and oxidising the product thus produced, a mixture of the two sulfones, $\text{H}_2\text{C}(\text{SO}_2\text{Me})_2$, m. 141°, and $\text{O}_2\text{S}(\text{CH}_2\text{SO}_2\text{Me})_2$, m. 184 to 185°, is obtained. The corresponding ethyl sulfones, $\text{H}_2\text{C}(\text{SO}_2\text{Et})_2$, m. 103°, and $\text{O}_2\text{S}(\text{CH}_2\text{SO}_2\text{Et})_2$, m. 149°, have been prepared in a similar way.⁴³ Reduction of carbon disulfide gave a product from which what appeared to be the methylene trithiocarbonate, $\text{H}_2\text{C}(\text{S}\cdot\text{CS}\cdot\text{SNa})_2$ was obtained.⁴²⁹ A derivative of methylene mercaptan has been patented.⁵⁴

Recently it has been found that *gem*-dithiols can be prepared, quite simply, in good yields and that they are relatively stable.¹¹⁰ The reactions may be represented as:



Aldehydes react at lower temperatures and pressures than ketones. Formaldehyde gives a 33% yield in 16 hours at 42° and 30 atmospheres pressure. Pressures up to 8000 atmospheres were used with ketones. Polymeric disulfides are by-products.

To avoid decomposition it is desirable to distil the *gem*-dithiols at reduced pressures so that they need not be heated above 80°, though some of them will stand higher temperatures. Some *gem*-dithiols can be stored for a year with little decomposition. They show typical mercaptan reactions. They form metal mercaptides and can be alkylated and acylated. The addition products with ethylene and propylene are mercaptals.

Ethylene mercaptan, prepared from ethylene chloride and potassium sulfhydrate back in 1840,³⁹³ is the only well known member of this class. Ethylene bromide and sodium hydrosulfide gave

it also.⁶⁵⁴ Ethylene mercaptan was obtained by the action of ammonia on polymeric ethylene trithiocarbonate.³⁰³ From alcoholic potassium hydroxide saturated with hydrogen sulfide and ethylene bromide, a 70% yield has been claimed.^{191a} Much lower yields have been reported.^{422, 595} One difficulty in getting a high yield is the formation of by-products. In one experiment about 16% of $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$, 1.5% of $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{-SCH}_2\text{CH}_2\text{SH}$ and about 10% of polymers were reported.⁴¹⁷ The polymers may have bromine terminals and molecular weights as high as 3000.⁵⁰² The formation of sulfide-mercaptans can be cut down by carrying out the reaction in an autoclave, under hydrogen sulfide pressure. Ethylene mercaptan may be prepared from sodium thiosulfate.²³⁹ The sodium amalgam reduction²¹⁷ or hydrogenation over a sulfactive catalyst³⁶⁸ of polymeric ethylene disulfides has been used.

It can be made by the thiourea process,^{7, 412a, 576} but with some difficulty. Ethylene bromide reacts promptly and vigorously with thiourea and the isothiuronium salt is obtained in high yield. For some reason this salt is not decomposed readily by alkali. Refluxing for 5 hours with 15 moles of potassium hydroxide appears to be necessary.⁵⁷⁶ This is seven times as much alkali and ten times as long as would be expected. This difficulty is not encountered when the reactive groups are further separated. The sulfide dimercaptan has been observed as a by-product.^{412a}

Trimethylene mercaptan, $\text{HSCH}_2\text{CH}_2\text{CH}_2\text{SH}$, has been prepared from the bromide and potassium hydrosulfide,^{17, 260, 412a, 503, 549, 566} by the thiourea method^{266, 412a} and also by reducing trimethylene thiocyanate, $\text{CH}_2(\text{CH}_2\text{SCN})_2$, with zinc and hydrochloric acid.²⁶⁰ The dimethyl-trimethylene mercaptan, $\text{HSCH}_2\text{-CMe}_2\text{-CH}_2\text{SH}$, has been prepared.²⁴ Propylene dimercaptan, $\text{CH}_3\text{CH}(\text{SH})\text{CH}_2\text{SH}$, b. 152° , and isobutylene dimercaptan have been made. The yield of the second was very poor.^{260, 566} The preparation and properties of a complete series of dimercaptans, up to dodecamethylene, have been described.²⁶⁶

For making the polymethylene mercaptans, the usual methods are available. A novel way is to prepare the bisdithiourethanes, $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CS}\cdot\text{S}(\text{CH}_2)_n\text{S}\cdot\text{CS}\cdot\text{NC}_5\text{H}_{10}$, from piperidine, carbon disulfide, and the dihalide. Treating this with alkali liberates the dimercaptan.^{91a}

Dimercaptans show the usual reactions of mercaptans. The

chief interest in the lower members has been in the formation of cyclic compounds. Many cyclic mercaptals have been prepared from ethylene mercaptan and the saccharides,^{366, 643} as well as from simpler aldehydes^{16, 191a, 191b} and from ketones.^{15, 191b, 239} These are described under mercaptals and under cyclic sulfides.^{417, 627}

Dimercaptans are said to be less toxic to catalysts than the monomercaptans.⁴¹⁵

One trimercaptan is known: trithioglycerol, $\text{HSCH}(\text{CH}_2\text{SH})_2$,^{111, 426, 516} which is insoluble in water but mixes with ether.

The mercaptan, $\text{C}(\text{CH}_2\text{SH})_4$, corresponding to pentaerythritol has been prepared by the catalytic hydrogenation of a polymeric polysulfide.^{190b}

It is claimed that polymers containing free mercaptan groups can be obtained by adding thioacetic acid to unsaturated polymers and hydrolyzing.³¹²

Comparison of Mercaptans with Alcohols, Hydrocarbons, and Alkyl Halides

In tables 2.1 to 10.1 and in most of the plots the mercaptans and alcohols are compared with the hydrocarbons having one more carbon atom, that is, ethyl mercaptan and ethanol are compared with propane, and so on, for the higher members. In this way there are the same number of heavy atoms in the compounds in each line. The secondary mercaptans and alcohols, $\text{RCH}(\text{SH})\text{CH}_3$ and $\text{RCH}(\text{OH})\text{CH}_3$, are compared with hydrocarbons of the structure $\text{RCH}(\text{CH}_3)\text{CH}_3$.

In the textbooks the statement is made that mercaptans boil lower than the alcohols. That is quite true for the lower ones; methyl and ethyl mercaptans boil at 58.5° and 43.6° , respectively, below methanol and ethanol, but the differences become less as the carbon chains become longer until the seventh members of the series are reached, and above that the mercaptans boil higher than the corresponding alcohols. With the secondary mercaptans and alcohols, the relations are nearly the same but not so regular. For comparison, the boiling points of the mercaptans, alcohols, hydrocarbons, and alkyl bromides are given in Table 2.1, with their differences, and those of the mercaptans, alcohols, hydrocarbons, and alkyl chlorides are plotted in Figures 1.1 and 2.1 against the number of carbon atoms. Columns 1, 5 and 8 give the boiling

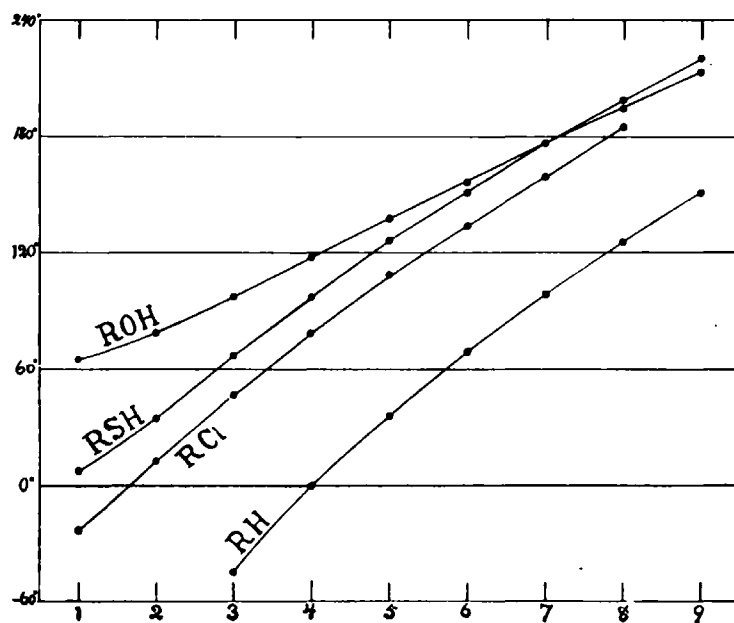


FIGURE 1.1. Boiling Points of Primary Mercaptans, Alcohols, Alkyl Chlorides and Hydrocarbons, Plotted against Number of Carbon Atoms

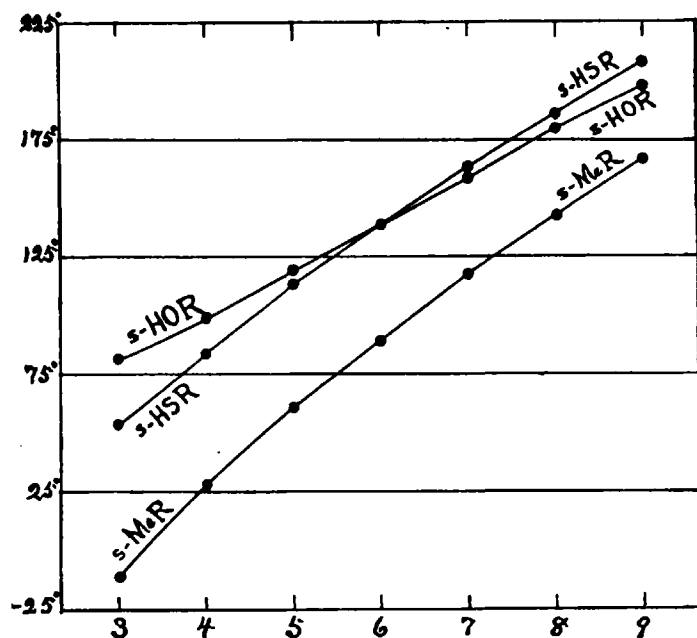


FIGURE 2.1. Boiling Points of Secondary Mercaptans, Secondary Alcohols and Hydrocarbons Plotted against Number of Carbon Atoms

points of the mercaptans, alcohols, and alkyl bromides. Column 7 gives the boiling points of the hydrocarbons, RMe. Thus line 1 has the boiling point of ethane, Me-Me, contrasted with those of Me-SH, Me-OH and Me-Br. Column 2, SH-Me, shows the elevation of the boiling point when sulfhydryl is substituted for methyl. Thus in line 1 the boiling point of methyl mercaptan, 6°, is 94.3° higher than that of propane. Column 6 shows the elevations when hydroxyl is substituted for methyl. Column 3 gives the differences between the alcohols and mercaptans. Methanol boils 58.5° above methanethiol while heptanol and heptanethiol boil at practically the same temperature.

TABLE 2.1

Boiling Points of Mercaptans Compared with Those of Alcohols, Alkyl Bromides and Hydrocarbons

No.	1 RSH	2 SH-Me	3 OH-SH	4 Br-SH	5 ROH	6 OH-Me	7 RMe	8 RBr
1	5.96	94.3	58.5	-2.4	64.5	152.8	-88.3	3.6
2	34.7	79.2	43.6	3.7	78.3	122.8	-44.5	38.4
3	67.5	68.0	29.7	3.5	97.2	97.7	-0.5	71.0
4	98.0	62.8	19.7	3.6	117.7	81.7	36.0	101.6
5	126.5	57.8	11.4	3.2	137.9	69.2	68.7	129.7
6	151.5	53.1	5.0	3.8	156.5	58.1	98.4	155.3
7	176.2	50.6	-0.1	3.8	176.3	50.7	125.6	180.0
8	199.1	48.4	-4.4	2.4	194.7	44.0	150.7	201.5
9	220.1	46.0	-6.6		213.5	39.4	174.1	
<i>Iso-compounds</i>								
4	88	60	19.9	3.4	107.9	80.0	27.9	91.4
5	119	59	13.0	1.6	132.0	71.7	60.3	120.6
<i>Secondary</i>								
3	52.9	64.6	29.4	-6.4	82.3	94.0	-11.7	59.35
4	84.5	56.6	15.0	-6.8	99.5	71.6	27.9	91.3
5	112.9	52.6	6.9	-0.1	119.8	59.5	60.3	113
6	138.9	48.8	0.9	-5.6	139.8	49.7	90.1	144
7	163.6	45.5	-4.9	-2.4	158.7	40.6	118.1	166
8	186.4	43.2	-7.4	-2.6	179.0	35.8	143.25	189
9	208.2	41.4	-9.9	0.2	198.3	31.5	166.8	208
<i>Tertiary</i>								
4	64	54.6	18.9	-9.3	82.86	45.9	9.45	73.3
5	98	49.3	4.3	-11.2	102.3	52.6	49.7	109.2

In Figure 3.1, the boiling points of the mercaptans, alcohols, hydrocarbons, and alkyl chlorides are plotted against their molecular weights. The hydroxyl group has a great effect but this falls off as the carbon chain lengthens. The elevation of the boiling point by the $-SH$ group diminishes slightly from methyl to amyl and then becomes practically constant. The boiling points of the secondary mercaptans bear a similar relation to those of the 2-methyl hydrocarbons. The alkyl chlorides boil almost exactly where hypothetical hydrocarbons of the same molecular weight would.

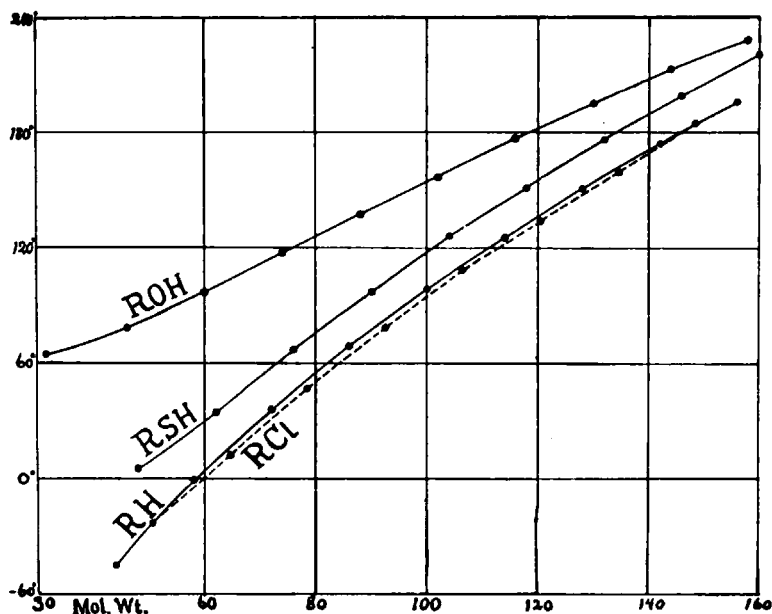


FIGURE 3.1. *Boiling Points of Primary Mercaptans, Alcohols, Alkyl Chlorides and Hydrocarbons Plotted against Molecular Weight*

The elevation of the boiling point by the mercapto group is partly due to its nature and partly to its weight. An attempt has been made, in Table 3.1, to evaluate these separately by taking the differences between the boiling points of the mercaptans and those of hypothetical hydrocarbons of the same molecular weights. The boiling points of these hypothetical hydrocarbons were read off from a plot of the boiling points of the normal hydrocarbons and the mercaptans against molecular weights. The results are in the column headed *Elevation*. The

same has been done for the alcohols. The column T/T' gives the ratios of the boiling temperatures of the mercaptans to those of the hypothetical hydrocarbons, both in degrees Kelvin. The same has been done for the alcohols.

TABLE 3.1
Association of Mercaptans

Mercaptans							Alcohols				
No.	Eleva- B.p. tion		T/T'	M.w.hc.	r	Asso.	Eleva- B.p. tion		T/T'	M.w.hc.	r
1	5.96	37.8	1.165	60.6	1.26	—	64.5	146.5	1.766	84.3	2.63
2	34.7	24.7	1.086	71.5	1.15	—	78.3	116.0	1.493	90.6	1.97
3	67.5	22.1	1.066	85.5	1.12	1.113	97.2	92.2	1.332	99.5	1.66
4	98.0	20.7	1.058	99.9	1.11	1.094	117.7	77.0	1.192	110.0	1.48
5	126.5	20.3	1.052	113.7	1.10	1.089	137.9	65.0	1.187	121.0	1.37
6	151.5	18.6	1.045	128.6	1.09	1.076	156.5	54.0	1.142	131.6	1.29
7	176.2	18.9	1.043	143.6	1.09	1.064	176.3	47.0	1.117	143.7	1.24
8	199.1	18.9	1.041	158.3	1.08	1.049	194.7	40.2	1.094	155.5	1.20
9	220.1	18.3	1.037	172.8	1.08	1.030	213.5	36.0	1.080	168.2	1.17
Ph	169.5	25.5	1.062	139.3	1.26	—	182.2	67.6	1.175	147.4	1.57

Secondary

3	52.9	15.7	1.050	82.8	1.09	1.095	82.3	88.5	1.331	96.4	1.60
4	84.5	15.6	1.045	97.2	1.08	—	99.5	67.0	1.181	104.8	1.41
5	112.9	14.8	1.037	111.5	1.07	1.039	119.8	55.0	1.162	115.0	1.31
6	138.9	13.6	1.032	125.5	1.06	1.032	139.8	45.2	1.123	126.1	1.23
7	163.6	13.7	1.032	140.3	1.06	1.025	158.7	36.2	1.091	137.2	1.18
8	186.4	13.2	1.029	153.9	1.05	1.012	180.0	33.2	1.082	150.6	1.16
9	208.2	13.4	1.025	168.1	1.05	1.000	198.3	28.2	1.064	162.9	1.13

The molecular weights of hypothetical hydrocarbons having the same boiling points as the mercaptans have been calculated and are listed under *M.w.hc.* The ratios of these to the molecular weights of the mercaptans are under *r*. This ratio is a sort of measure of the association of the mercaptans. For the primary mercaptans this ratio starts at 1.27 and decreases until it becomes practically constant at 1.08. It is 0.03 lower for any secondary than for the corresponding primary. Under *Asso.*, figures are given for the association calculated from fluidities.^{67a} There is close agreement. Corresponding data are given for the alcohols. Thiophenol is more like a lower primary mercaptan.

In physical properties, except densities, mercaptans resemble alkyl bromides and hydrocarbons closely. As far as boiling points are concerned, the substitution of the $-SH$ group in a hydrocarbon

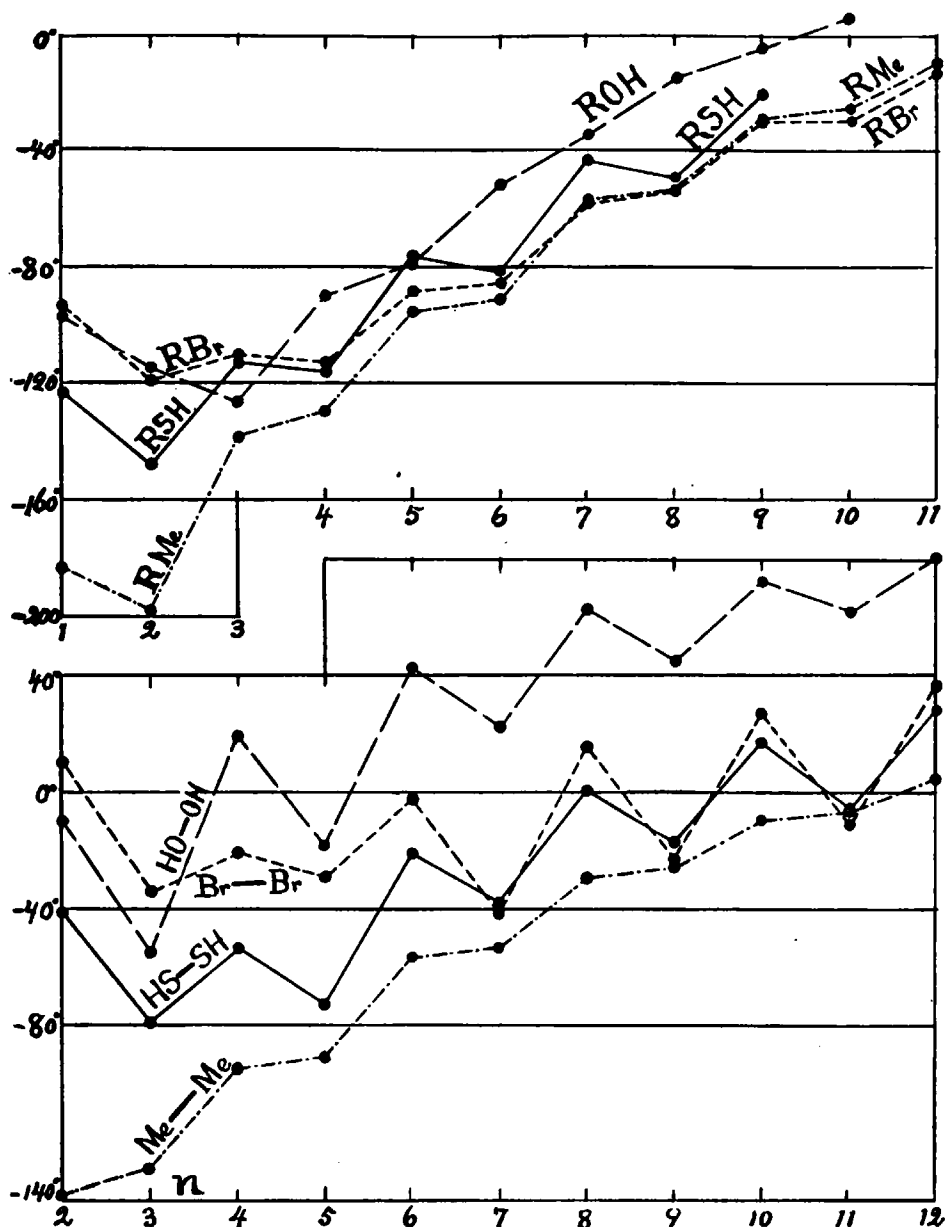


FIGURE 4.1. Upper Part: Melting Points of Mercaptans, Alcohols, Bromides and Hydrocarbons Plotted against Number of Carbon Atoms

Lower Part: Melting Points of Dimercaptans, Glycols, Dibromides and Hydrocarbons Plotted against Number of Carbon Atoms

has practically the same effect as that of a bromine atom. This is true also for the secondary and tertiary compounds. As seen in column 4 of Table 2.1, the boiling points of the primary mercaptans, from ethyl to hexyl, average 3.6° lower than the corresponding alkyl bromides. The melting-point pattern of the mercaptans, as seen in the upper part of Figure 4, is much like that of the alkyl bromides, which closely resembles that of the hydrocarbons, RMe, having the same numbers of heavy atoms. Data on solubilities in water of these compounds are scanty, but such figures as are available indicate that the solubilities of butyl mercaptan, butyl bromide, and pentane are of the same order (see Table 4.1).

TABLE 4.1

*Solubilities of Mercaptans, Bromides, and Hydrocarbons in Water
(in grams per liter of water at 20 to 30°)*

R	RSH	RBr	RMe
Me	23.300	—	—
Et	6.760	8.96	—
Pr	1.960	2.31	—
Bu	0.570	0.61	0.360
Am	0.164	—	0.140
Hex	0.043	—	0.052
Hep	0.014	—	0.015

In Figure 5.1, the densities of the primary and secondary mercaptans are plotted along with those of the corresponding alcohols. There is a sharp drop from methyl to ethyl on account of the decrease in the percentage of sulfur. From ethyl the density rises slowly. The increase in density due to the higher percentage of carbon is largely compensated by the decrease in sulfur content.

The melting points of primary mercaptans, alcohols, alkyl bromides, and hydrocarbons are given in Table 5.1 for comparison. The similarities are closer if propane is put with ethyl mercaptan, ethyl alcohol and ethyl bromide, and so for the higher members of the series. The melting points are more alike when the molecules have the same number of heavy atoms rather than the same number of carbons.

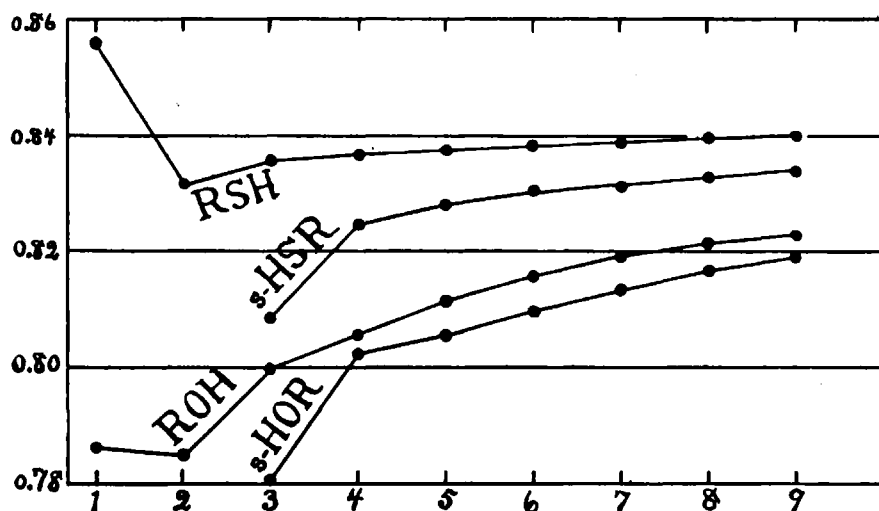


FIGURE 5.1. Densities, 25/4, of Primary and Secondary Mercaptans and Alcohols, Plotted against Number of Carbon Atoms

TABLE 5.1

Melting Points of Mercaptans, Alcohols, Alkyl Bromides, and Hydrocarbons Having Like Numbers of Heavy Atoms

R	RSH	ROH	RBr	Rme
Me	-123.0	- 97.0	- 93	-183.2
Et	-147.3	-114.6	-119.0	-187.7
Pr	-113.3	-126.1	-110.0	-138.3
Bu	-115.9	- 89.8	-112.4	-129.7
Am	- 75.7	- 78.5	- 88.0	- 95.3
Hex	- 81.0	- 51.6	- 85.0	- 90.6
Hep	- 43.4	- 34.1	- 38.9	- 56.8
Oct	- 49.2	- 15.0	- 54.0	- 53.7
Non	- 20.1	- 5.0	- 30.8	- 29.7
Dec	—	6.0	- 29.6	- 25.6
Und	—	15.8	- 13.1	- 9.6
Dod	—	23.9	- 9.6	- 6.2

These data are plotted in the upper part of Figure 4.1, from which it is seen that the melting points of the alcohols make a pattern that is entirely different from those of the mercaptans,

bromides, and hydrocarbons. The patterns for RSH, RBr, and RMe are very similar.

The melting points of the 2-mercapto and the 2-methyl hydrocarbons are in Table 6.1.

TABLE 6.1

Melting Points of 2-Mercapto- and 2-Methyl-Hydrocarbons

	$\text{RCH}(\text{SH})\text{CH}_3$	$\text{RCH}(\text{Me})\text{CH}_3$
Propane	-130.7	-145.0
Butane	-165.0	-160.9
Pentane	-169.0	-160.5
Hexane	-147.0	-155.0
Heptane	-141.0	-111.3
Octane	- 79.0	- 80.0
Nonane	- 69.0	- 74.7

These are plotted in Figure 6.1. There is a similarity in the two melting point patterns, though they are close together only a part of the way.

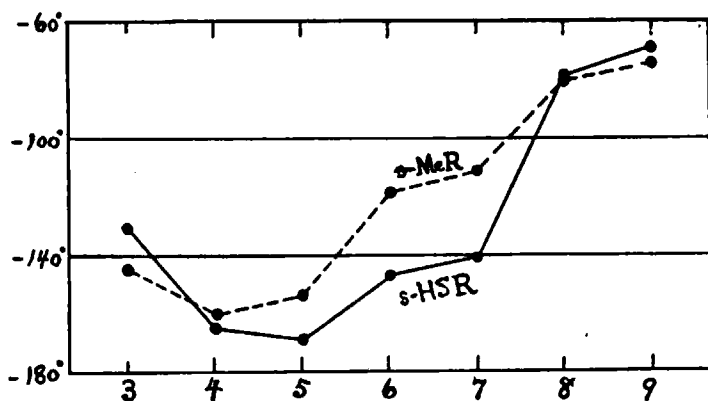


FIGURE 6.1. *Melting Points of 2-Mercapto- and 2-Methyl-Hydrocarbons, Plotted against Number of Carbon Atoms*

As for the monomercaptans in Table 3.1, in Table 7.1 data are given for the boiling points of the dimercaptans and glycols. Unfortunately, the available data for the glycols are scanty and, except for the first two, not very accurate.

TABLE 7.1
Association of Dimercaptans

Dimercaptans						Glycols				
No.	B.p.	Eleva- tion	T/T'	M.w.hc.	r	B.p.	Eleva- tion	T/T'	M.w.hc.	r
2	146.0	60.2	1.168	125.5	1.33	197.4	187.5	1.663	157.3	2.53
3	172.9	58.9	1.153	141.5	1.31	214.0	168.8	1.530	168.6	2.22
4	195.6	55.6	1.134	156.1	1.28	230.0	153.0	1.445	180.2	2.00
5	217.3	53.2	1.122	170.9	1.26	239.0	133.0	1.350	186.2	1.79
6	237.1	50.6	1.110	185.3	1.23	250.0	117.0	1.290	195.5	1.65
7	252.2	44.7	1.093	197.2	1.20	262.0	105.0	1.243	205.0	1.55
8	269.3	42.0	1.083	210.9	1.18					
9	284.0	38.1	1.073	223.7	1.16					
10	297.1	33.5	1.062	235.0	1.14					
11	308.8	28.8	1.053	245.7	1.12					
12	319.3	23.3	1.043	255.3	1.09					

Table 8.1 lists the elevations of the boiling point of a hydrocarbon caused by the introduction of the first and second -SH or -OH groups.

TABLE 8.1
Elevation of Boiling Point by First and Second Substitutions of SH Groups

	1st SH	2nd SH	1st OH	2nd OH
Ethane	123.0	111.3	166.7	118.8
Propane	112.5	104.9	141.7	116.8
Butane	98.5	97.6	118.2	112.3
Pentane	90.5	90.8	101.8	101.6
Hexane	82.8	85.6	87.8	93.5
Heptane	77.8	76.0	77.9	82.7
Octane	73.5	70.2	69.1	—
Nonane	69.5	63.8	62.8	—

With ethane and propane, the introduction of the second -SH or -OH group has less effect than that of the first, but for the higher hydrocarbons there is little difference. The figures in the

literature for the boiling points of the higher glycols at atmospheric pressure are probably not accurate.

Monothioglycol, $\text{HSCH}_2\text{CH}_2\text{OH}$, boils at about 160° . The introduction of the $-\text{SH}$ group into ethanol raises the boiling point 88° , while the substitution of $-\text{OH}$ for a hydrogen of ethyl mercaptan raises the boiling point 154° .

The melting points of polymethylene dimercaptans, glycols, and dibromides are given in Table 9.1, along with those of the $n + 2$ hydrocarbons. As with the mono-derivatives, it seems best to contrast compounds having the same number of heavy atoms.

TABLE 9.1

Melting Points of Polymethylene Compounds

No.	HS-SH	HO-OH	Br-Br	Me-Me
2	-41.2	-11.2	10.0	-138.3
3	-79.0	-55.0	-34.2	-129.7
4	-53.9	19.5	-21.1	-95.4
5	-72.5	-18.0	-29.5	-90.6
6	-21.0	42.8	-2.3	-56.8
7	-38.1	22.5	-41.7	-53.7
8	0.9	63.0	16.0	-29.7
9	-17.5	45.8	-22.5	-25.6
10	17.8	72.5	27.4	-9.6
11	-5.4	62.2	-10.6	-6.2
12	28.4	80.8	36.8	5.5

These are plotted in the lower part of Fig. 4.1. The melting points of the glycols form a pattern which is very different from those of the other series. The patterns of the dimercaptans and dibromides are strikingly alike. From hexamethylene on up the melting points of the dibromides are alternately above and below those of the mercaptans. Starting with heptamethylene, any dimercaptan, the corresponding dibromide and the hydrocarbon, $n + 2$, melt at very nearly the same temperature.

There are selenium,^{554, 564} and tellurium⁶⁷² compounds corresponding to the mercaptans but they are not well known. The boiling points are given in Table 10.1, along with those of the mercaptans.

TABLE 10.1
Boiling Points of RSH, RSeH¹²⁴ and RTeH³⁷

Alkyl	RSH	Difference	RSeH	Difference	RTeH
Methyl	6.0	6.0	12.0 ³⁷	45.0	57
Ethyl	34.7	18.8	53.5	36.5	90
Propyl	67.5	16.5	84.0	37.0	121
Butyl	98.0	16.0	114.0	37.0	151

The boiling point given for methyl selenomercaptan appears to be too low a figure; nearer to 20° would look better. Other data are: EtSeH d 24/4 1.3954, n_D 1.47715; PrSeH d 20/4 1.3020, n_D 1.47560; BuSeH d 24.5/4 1.2352, n_D 1.47446; ¹²⁴ i-PrSeH b. 70 to 75°; ⁴⁴¹ DecSeH b_{13} 128 to 129°; ⁹⁶ cyclohexaneselenol b. 170 to 172°, d_0 1.1223.⁴⁰⁵

Physical Properties of Mercaptans

Many studies have been made of the physical properties of mercaptans, frequently for comparison with alcohols. The heats of combustion and of formation have been measured for several mercaptans.^{59, 66, 617} The data have been summarized and discussed. The heat of formation of the C-S linkage is greater in the sulfides than in the corresponding mercaptans and still greater in carbon disulfide.⁶⁰¹ The valence force potentials in methyl mercaptan and in methyl sulfide are only slightly different.⁵⁶² The possibility of resonance structures has been considered.⁶⁵³

Cryoscopic measurements^{18, 567} and the Trouton constants⁶¹⁴ indicate no association. The fluidities of a series of mercaptans have been compared with those of the alcohols.^{67a, 67b} They likewise show that the association is low; it decreases as the number of carbon atoms increases. The fluidity at any temperature is given by the equation:

$$\log \nu = A + B/2.03 \text{ RT.}$$

The constants A and B are characteristic of individual mercaptans.³⁸⁹ The parachors of alcohols indicate association, while those of the mercaptans do not.⁵⁶⁷

The refractivities and parachors of a number of mercaptans have been determined.⁶³⁷ The refractivities of the isomeric propyl and butyl mercaptans have been determined for nine wave lengths.^{412c}

The refractive index of a normal primary mercaptan, from ethyl to nonyl, is given by the equation:

$$n_{25/D} = 1.4720 - 0.2190/(C + 2.881)$$

C is the number of carbon atoms. For the secondary, from *s*-butyl to *s*-nonyl, the equation is:

$$n_{25/D} = 1.4730 - 0.2759/(C + 3.075).^{153}$$

The mean values for atomic refractivity of sulfur have been given as r_a 7.63, r_D 7.69, r_β 7.83, r_γ 7.98.^{490b} From all available data, the atomic refractivity of sulfur in mercaptans has been calculated by three methods. The value proposed is 7.766 ± 0.011 .^{412b} Another survey gives 7.81 ± 0.04 for aliphatic and 8.56 for aromatic.⁸⁴

The heat of vaporization of methyl mercaptan, as a function of temperature and pressure, has been compared with data for other compounds.²⁶¹

The effect of a sulfur atom on the magnitude of optical rotation^{98, 382, 687} and whether or not a Walden inversion³³¹ takes place during the introduction of a mercapto group have been studied. The rotations of the sulfonic acids from the oxidation of MePhCHSH, EtPhCHSH, *i*-PrPhCHSH and BuPhCHSH are opposite to those of the mercaptans.^{380e}

The surface tension of ethyl mercaptan is much less than that of alcohol.^{272, 273} The densities and dielectric constants of benzene solutions of the isomeric propyl and butyl mercaptans have been measured.^{412d}

The polarographic behavior of the -SH group has been studied. *p*-Thiocresol gives two anodic waves between pH 2 and pH 12 in propanol-2.⁵³²

Appearance potentials have been determined for several gaseous ions formed by electron impact on ethyl, propyl, and *t*-butyl mercaptans.²¹⁶

In the infrared, mercaptans have a well-defined absorption band at 3.8μ ⁵¹ or at 3.85 .^{90, 662} Other bands have been noted at 2.00μ ,¹⁸³ at 2.27 and 2.92.²³⁸ Tables are given for the positions

of the absorption bands due to the S-H of different mercaptans.^{248, 624} The infrared absorption and diffusion spectra show that the C-S and C-O bonds in methyl mercaptan and methanol are highly polarized, giving high dipole moments.^{165a} The wave lengths of the observed bands have been correlated with the known Raman frequencies.⁶¹⁵ The bond-stretching frequencies for RSH are lower when R is $t\text{-Bu}$, $\text{CH}_2\text{:CHCH}_2$ or PhCH_2 , than when R is a saturated alkyl.⁵⁵⁵ The presence of sulfur in a molecule does not affect the observed frequencies greatly.⁴⁸⁸

There have been many studies of the ultraviolet absorptions of mercaptans.^{31, 76, 89, 230a, 346, 428, 491, 612, 613} The extinction curve for ethyl mercaptan begins at about $300\ \mu\mu$ and has a maximum at about 185 .⁴³¹ There are bands at $193.5\ \mu\mu$ and at 225 .³⁸⁶ The energies of dissociation of some mercaptans have been calculated from the edge of the continuous absorption in the ultraviolet.^{230b} The absorption by thiophenol in ethanol is altered greatly by the addition of sodium ethylate.²¹²

The dispersion equivalent of sulfur in mercaptans has been compared with its value in other sulfur compounds.²⁴⁷

The Raman spectra of a number of mercaptans show the frequency shifts of 2573, 739, and 657, of which 2573 is attributed to the S-H oscillation and the other two to the oscillations of the C-S . The 2573 shift has been observed in hydrogen sulfide.⁶³⁴ Mercaptans and other sulfur compounds show characteristic frequencies.¹⁴² Photographs have been made of the spectra of methyl,^{185, 638, 644a} ethyl,^{638, 644b} n -propyl,⁴⁹⁷ i -propyl,^{150a, 497} n -butyl,³²⁵ s -butyl, t -butyl,³⁵⁰ n -amyl,^{150b} i -amyl,^{150b, 610} t -amyl,³⁵⁰ cyclopentyl,³⁵¹ phenyl,^{130, 326, 349, 351, 352, 418, 533, 670} and benzyl.⁵⁰⁹ The spectra of EtSH and EtSD have been compared.²⁸⁴

Dipole moments of a number of mercaptans have been measured and compared with those of alkyl sulfides, alcohols and ethers.^{300a, 300b, 459, 648, 674} The moments of alkyl sulfides are lower than those of the corresponding ethers, but with the mercaptans and alcohols, this is reversed. The diamagnetic susceptibilities have been used as a means of determining structure.^{131, 143} The dielectric constant of ethyl mercaptan vapor has been determined.³⁶²

The ionization constants of mercaptans are of the order of 10^{-11} .³⁵³ The pK values of several are: phenyl 8.3, benzyl 11.8,

ethyl 12.0, hexyl 13.5, octyl 13.8, and dodecyl 13.8.⁴¹⁴ The acidities of thiophenol and of several substituted thiophenols have been determined in 60 and in 100% ethanol.^{547, 548} Their acidities are about two hundred times as great as those of the corresponding phenols.⁵⁴⁸ A more elaborate comparison has been made.⁵⁵⁰ Butyl, phenyl, and tolyl mercaptans show no conductivity in liquid hydrogen sulfide.⁴⁹⁵

Solutions of thiols in concentrated sulfuric acid are deeply colored and show paramagnetic absorptions. Certain similarities have been observed in all the thio compounds, indicating that similar species in all of them contribute to the paramagnetism.²⁸³

Mercaptans form azeotropes with some hydrocarbons but not with others.²⁹⁰ The data in Table 11.1 are taken from recent studies.^{156, 159, 290, 371b} Some azeotropes with alcohols³⁵⁹ and a ketone^{371a} are in Table 12.1.

Azeotropes have been used in the separation of mercaptans and alcohols.³⁷⁹ Completely fluorinated organic compounds have been recommended for the azeotropic separation of mercaptans from hydrocarbons.¹²⁵

TABLE 11.1
Azeotropes with Hydrocarbons

Mercaptan	B.p. °C	Hydrocarbons	B.p. °C	Azeotrope	
				B.p. °C	RSH %
Methyl	6.00	<i>i</i> -Butane	-11.70	-13.00	14.9 ⁹⁹
Ethyl	35.04	<i>i</i> -Pentane	27.90	25.72	29.0
		<i>n</i> -Pentane	36.15	30.46	51.0
		2-Methyl-2-butene	37.20	33.00	60.0
		Cyclopentane	49.35	34.95	89.0
		Neohexane	49.70	34.41	83.0
<i>n</i> -Propyl	67.82	<i>i</i> -Hexane	60.40	59.20	23.9
		2,3-Dimethylbutane	58.10	57.50	16.3
		<i>n</i> -Hexane	68.75	64.35	52.6
		Methylcyclopentane	71.85	66.45	64.2
		Neoheptane	79.20	67.20	81.3
		2,2,3-Trimethylbutane	80.80	67.60	87.4
		Cyclohexane	80.85	67.77	97.6
		Cyclopentane	49.35	47.75	35.3
<i>i</i> -Propyl	52.60	Neohexane	49.70	47.41	37.7
		2,3-Dimethylbutane	58.10	51.24	67.5
		<i>i</i> -Hexane	60.40	51.70	75.9
		3-Methylpentane	63.35	52.40	87.0

TABLE 11.1 (Continued)

Mercaptan	B.p. °C	Hydrocarbons	B.p. °C	Azeotrope	
				B.p. °C	RSH %
<i>n</i> -Butyl	98.58	2,3-Dimethylpentane	89.90	89.50	15.1
		<i>i</i> -Heptane	90.10	89.74	15.4
		<i>trans</i> -1,3-Dimethyl- cyclopentane	90.80	90.50	12.7
		<i>cis</i> -1,2-Dimethyl- cyclopentane	99.60	96.30	52.0
		3-Methylhexane	91.60	91.20	22.8
		<i>n</i> -Heptane	98.40	95.45	49.4
		2,2,4-Trimethylpentane	99.30	95.50	50.3
		Methylcyclohexane	101.00	97.00	58.2
		Ethylcyclopentane	103.40	97.80	72.1
		Neooctane	106.80	98.01	78.8
		2,5-Dimethylhexane	109.10	98.20	88.0
		3,3-Dimethylhexane	112.20	98.60	97.6
<i>s</i> -Butyl	85.15	Neohexane	79.20	78.60	23.1
		2,4-Dimethylpentane	80.50	79.50	28.1
		Cyclohexane	80.85	79.97	25.5
		1,1-Dimethylcyclopentane	87.90	83.90	64.1
		2,3-Dimethylpentane	89.90	84.20	68.6
		<i>i</i> -Heptane	90.10	84.30	72.1
		3-Methylhexane	91.60	84.70	80.8
		<i>trans</i> -1,3-dimethylcyclo- pentane	90.80	84.70	78.1
<i>i</i> -Butyl	88.72	Neohexane	79.20	79.10	10.3
		2,4-Dimethylpentane	80.50	80.30	14.1
		Cyclohexane	80.80	80.70	11.7
		2,2,3-Trimethylbutane	81.00	80.60	16.4
		1,1-Dimethylcyclopentane	87.90	85.70	44.2
		2,3-Dimethylpentane	89.90	86.30	54.1
		<i>trans</i> -1,3-Dimethylcyclo- pentane	90.80	87.00	58.6
		<i>cis</i> -1,2-Dimethylcyclo- pentane	99.60	88.50	98.6
		3-Methylhexane	91.60	87.20	62.8
		Heptane	98.40	88.50	91.3
		2,2,4-Trimethylpentane	99.30	88.40	90.0
<i>t</i> -Butyl	64.35	2,3-Dimethylbutane	57.80	56.10	21.1
		<i>i</i> -Hexane	60.40	59.50	30.4
		3-Methylpentane	63.30	61.50	46.5
		Hexane	68.70	63.80	75.8
		Methylcyclopentane	71.80	64.40	95.3
		With other compounds			
Ethyl	35.04	Ether	34.60	31.50	40.0
		Methyl formate	31.90	27.00	70.0
		<i>i</i> -Propyl chloride	36.30	36.20	45.0

TABLE 12.1
Azeotropes with Alcohols and a Ketone

	RSH B.p., °C	ROH B.p., °C	Azeotrope B.p., °C	% RSH
Propyl	67.5	97.4	66.2	91.35
Butyl	98.0	117.0	97.4	85.16
<i>i</i> -Amyl	118.0	132.0	115.3	77.11
	RSH	MeCOEt		
Propyl	67.5	79.6	65.5	75.00

Data for several properties of the primary mercaptans, from methyl to *n*-nonyl, and of the secondary, from *i*-propyl to *s*-nonyl, are in Tables 13.1, 14.1, and 15.1. The melting points,^{60a} boiling points, densities, indices of refraction,¹⁸⁴ and fluidities^{67b} were determined on the same samples. The dissociation constants are

TABLE 13.1
*Melting Points, Boiling Points and Densities
of Mercaptans*¹⁸⁴

Alkyl	M.p., °C	B.p., °C	d ₄ ²⁰	d ₄ ²⁰ , **	d ₄ ²⁵	Expansion 1° × 10 ³
Methyl	-123.0 ⁵²⁷	5.96 ⁵²⁷	0.8948	0.86689	0.85991	1.6239
Ethyl	-147.3	34.7 ⁸⁰	0.8617	0.83754	0.83147	1.4562
Propyl	-113.3	67.5	0.8617	0.84091	0.83572	1.2430
Butyl	-115.9	98.0*	0.8601	0.84122	0.83651	1.1261
Amyl	- 75.7	126.5	0.8595	0.84190	0.83750	1.0517
Hexyl	- 81.0	151.5	0.8591	0.84243	0.83826	0.9949
Heptyl	- 43.4	176.2	0.8589	0.84292	0.83891	0.9551
Octyl	- 49.2	199.1	0.8590	0.84344	0.83956	0.9252
Nonyl	- 20.1	220.2	0.8591	0.84393	0.84015	0.9008
<i>i</i> -Propyl	-130.7	52.9	0.83559	0.81393	0.80851	1.3397
<i>s</i> -Butyl	-165.0	84.5	0.84906	0.82948	0.82459	1.1870
<i>s</i> -Amyl	-169.0	112.9	0.85068	0.83269	0.82815	1.0969
<i>s</i> -Hexyl	-147.0	138.9	0.85217	0.83483	0.83050	1.0437
<i>s</i> -Heptyl	-141.0	163.6	0.85171	0.83525	0.83114	0.9900
<i>s</i> -Octyl	- 79.0	186.4	0.85281	0.83691	0.83292	0.9542
<i>s</i> -Nonyl	- 69.0	208.2	0.85313	0.83770	0.83384	0.9254

* Average of 97.3 and 98.7°.

** Calculated from d₄²⁰ and d₄²⁵.

from Yabroff.⁶⁷⁹ He determined the solubilities in water of the normal mercaptans, ethyl to amyl, and found that their logarithms, when plotted against the number of carbon atoms, lie on a straight line. The values given in the table were calculated from this line.

TABLE 14.1

Refractivity, Fluidity, and Solubility in Water of Mercaptans

Alkyl	n_D^{25}	MR		Fluidity at 20°	Solubility in Water at 20° grams/liter	$K \times 10^{11}$
		Found	Calculated			
Methyl	—	—	—	—	23.30	2.00
Ethyl	1.4270	19.19	19.13	333.5	6.76	2.52
Propyl	1.4351	23.77	23.74	247.4	1.96	2.26
Butyl	1.4401	28.41	28.36	200.3	0.57	2.21
Amyl	1.4440	33.04	32.98	154.7	0.164	2.00
Hexyl	1.4473	37.68	37.60	121.6	0.047	—
Heptyl	1.4498	42.33	42.22	94.7	0.0138	1.77
Octyl	1.4519	46.97	46.83	73.8	0.0040	—
Nonyl	1.4537	51.62	51.45	59.5	0.00115	—
<i>i</i> -Propyl	1.4223	23.97	23.74	265.4	—	—
<i>s</i> -Butyl	1.4338	28.46	28.36	—	—	—
<i>s</i> -Amyl	1.4386	33.06	32.98	183.7	—	—
<i>s</i> -Hexyl	1.4426	37.69	37.60	143.1	—	—
<i>s</i> -Heptyl	1.4452	42.35	42.22	111.5	—	—
<i>s</i> -Octyl	1.4481	47.00	46.83	86.9	—	—
<i>s</i> -Nonyl	1.4500	51.64	51.45	67.5	—	—

Secondary mercaptans are about 15% more fluid than primary mercaptans.

TABLE 15.1

*Boiling Points (°C.) of Mercaptans at Reduced Pressures*¹⁸⁴

No.	30 mm.	50 mm.	70 mm.	90 mm.	110 mm.	150 mm.	300 mm.
<i>Primary</i>							
5	—	—	57.7	—	68.7	76.7	95.9
6	—	72.4	—	86.4	—	99.7	120.1
7	81.2	—	101.2	—	—	121.6	142.9
8	99.8	—	120.6	—	—	142.1	164.0
9	117.4	—	138.7	—	—	160.8	184.1

TABLE 15.1 (*Continued*)

No.	30 mm.	50 mm.	70 mm.	90 mm.	110 mm.	150 mm.	300 mm.
<i>Secondary</i>							
5	—	—	—	—	55.9	63.9	83.6
6	—	60.6	—	74.2	—	87.5	107.3
7	69.6	—	89.2	—	—	109.5	130.4
8	88.9	—	109.1	—	—	130.1	151.7
9	106.8	—	128.1	—	—	149.9	172.4

The usually determined properties of a number of mercaptans are assembled in the following tables. Reference should be made to Tables 13.1 to 15.1 for certain properties of particular groups. All available data are given for each property of each mercaptan. This shows the state of our knowledge of that mercaptan; the references list the chemists who have prepared it. A study of the data in these tables reveals the sketchiness of our knowledge of physical properties. For only a few compounds have accurate determinations of physical properties been made. Credit for a compound is claimed by the first chemist who made it. Credit should go to the one who prepares a product of known purity and supplies accurate data on its physical properties. For any mercaptan, there are as many sets of data as there are authors. Small differences are to be expected in independent determinations of any property, but glaring discrepancies are frequent. We find two melting points, 32.5° and 56°, for octadecyl mercaptan. The higher one is probably the melting point of the disulfide which was mistaken for the mercaptan. This may be true in other cases.

Distillation temperatures, taken under unknown barometric pressure with any thermometer that may be handy and uncorrected, masquerade as "boiling points." At low pressures the "boiling points" are even less reliable, since the vapor pressures have little slope and a small error in reading the manometer vitiates the result. We find in the tables *n*-hexyl b_{90} 86.4° and b_{100} 84°, *n*-decyl b_2 96°, b_5 96° to 97° and oleyl $b_{0.05}$ 171° to 175° and $b_{0.2}$ 171° to 178°. Boiling points at pressures less than 1 mm. may have little meaning.

Densities are frequently given at odd temperatures as ethyl mer-

captan d 16.7/4 0.8428. The d_{21} 0.835 may mean d 21/21 or 21/4. It is impossible to compare such data with determinations at standard temperatures. It is desirable for densities to be given at two temperatures, 0/4 and 20/4 or 25/4, so that densities at other temperatures may be calculated. Discrepancies between determinations at the same temperature may be attributed to impurities in the samples. Thus for ethyl mercaptan, we find for d 25/4 0.83147 and 0.8373.

For many compounds there is a sad deficiency of data. Thus we find for 2-mercaptoisohexane only $[\alpha]_{20/D}$ 21.2°, for pentanethiol-3 only b_7 105° and for nonanethiol-5 only b_7 72°. Densities, but no refractive indices, are given for some compounds and vice versa for others.

Physical Properties of Aliphatic Mercaptans

Methyl, CH_3SH , m. -130.5° ,^{113, 635} -121.0° ,^{60, 618} -123.1° ,⁶⁰⁸ -123.0° ,⁵²⁷ b. 5.96° ,^{40, 527} 7.2° ,¹³⁸ 6° ,^{9, 12, 278c, 646b} b_{752} 5.8° ,^{19, 344b} b_{601} 0° ,¹⁵² b_1 -90.7° , b_5 -75.3° , b_{10} -67.5° , b_{20} -58.8° , b_{40} -49.2° , b_{60} -43.1° , b_{100} -34.8° , b_{200} -22.1° , b_{400} -7.9° , b_{760} 6.8° , b_{2at} 26.1° , b_{5at} 55.9° , b_{10at} 83.4° , b_{20at} 117.5° , b_{30at} 140.0° , b_{40at} 157.7° , b_{50at} 172.0° , b_{60at} 185.0° ; critical temperature 196.8° ; critical pressure 71.4 at.; T_{bp}/T_c 0.598;⁶⁰ vapor-pressure equation:⁵²⁷

$$\log p = 18.2749 - 1769.05/T - 3.70248 \log T$$

d 0/4 0.8961, d 26.3/4 0.8589, d 35.5/4 0.8472, d 49.7/4 0.8267, d 78/4 0.7840,⁶⁰ d 0/4 0.894.⁹ Heat of fusion 1411.4 cal./mole, heat of vaporization 5872 cal./mole, entropy 60.16 cal./degree/mole,⁵²⁷ 60.91 at 25° .⁴⁰ The heat of combustion at constant pressure is 298.81 cal. and the heat of formation 5.37, at constant volume 43.75.⁶¹⁷ A late value is -17.172 .⁶⁶ The heat capacity at 25° , 12.12 cal./degree/mole, and other properties have been determined.⁴⁰ The Raman spectrum has been studied^{644a} and valency forces and bond distances determined.^{165b, 219}

Ethyl, $\text{CH}_3\text{CH}_2\text{SH}$, m. -147.90° ,⁴⁰¹ -147.97° ,¹⁵⁶ -147.89° ,²⁶² -147.3° ,⁶⁰⁸ -147.0° ,⁶¹⁸ -144.4° ,^{113, 635} b. 35.00° ,^{262, 401} 35.04° ,¹⁵⁶ 34.7° ,⁶⁰ b_{752} 34.4 – 4.6° ,¹⁶⁴ b_{768} 35.3° ,^{300a} 36.2° ,^{19, 387b, 440, 646b, 646c} 33° ,⁶¹⁴ 36° ,^{278c, 646b} 37° ,^{12, 61a, 113, 635} 36.5 – 7° ,^{644b} b_1 -76.1° , b_5 -59.1° , b_{10} -50.2° , b_{20} -40.7° , b_{40} -29.8° , b_{60} -22.4° , b_{100} -13.0° , b_{200} 1.5° , b_{400} 17.7° , b_{760} 35.0° , b_{2at} 56.6° , b_{5at} 90.7° , b_{20at} 159.5° , b_{30at} 184.3° , b_{40at} 204.7° , b_{50at} 220° ; ⁶⁰ d 0/4 0.86174,¹⁸⁴ 0.8609,⁴³² 0.8623,⁶⁰ d 20/4 0.8375,¹⁵⁶ 0.83907,⁴⁴⁰ 0.8391,^{61a, 177} 0.83914,²⁶²

0.8398,^{300a} $d_{16.7/4}$ 0.8428,⁴⁹⁹ d_{21} 0.835,^{387b} d_{17} 0.845,^{686a, 686b} $d_{21/4}$ 0.8380,^{113, 635} $d_{25/4}$ 0.83147,¹⁸⁴ 0.8373,¹⁶⁹ 0.83316,²⁶² $d_{15.4/4}$ 0.8454, $d_{23.7/4}$ 0.8357, $d_{31.7/4}$ 0.8259, $d_{38.7/4}$ 0.8162, $d_{48.4/4}$ 0.8043, $d_{78.4/4}$ 0.7652;⁶⁰ $n_{20/D}$ 1.4318,¹⁵⁶ 1.43055,⁴⁴⁰ 1.4306,¹⁷⁷ 1.43119,^{300a} 1.43055,^{61a, 61b} $n_{25/D}$ 1.4270.¹⁸⁴ Critical temperature 206.9°,⁴⁹⁹ 228°,¹⁹⁶ 228.3°,⁶³⁵ 225.5°;⁶⁰ critical pressure 54.2 at.,⁶⁰ 63.5 at.;⁶³⁵ T_{bp}/T_c 0.616;⁶⁰ solubility in water 1.5 g./liter,²⁷² 7 g./liter at 20° or 0.112 moles/liter,⁶⁷⁹ 13 g./liter at 25°;²⁸⁴ surface tension 23.63 dynes/cm. at 2° and 21.62 at 16.7°,⁴⁹⁹ 21.82 at 20°.²⁷² At 99° the vapor density is 2.201 compared to air, calculated 2.144.¹⁶⁸ Explosive limits 2.8 and 18.2% by volume of vapor; minimum ignition temperature 299° in air, 261° in oxygen.³²² The Trouton constant indicates no association.⁶¹⁴ The association at boiling point is 1.23.^{646c} The heat of formation is 19.5 cal.,⁵⁹ 13.27 at constant pressure and 90.03 at constant volume.⁶¹⁷ The heat of combustion is 455.65 cal. at constant pressure.⁶¹⁷ At 25° the entropy is 70.6 cal./degree/mole and the heat capacity 17.6 cal./mole.⁴⁰ The heat of vaporization is 6860 cal.⁶¹⁴ The diamagnetic susceptibility is 46.97.¹²⁹ The dielectric constant is 7.95 and the association factor 1.04.^{499, 646a} Its dipole moment in benzene at 15° is 1.38×10^{-18} ,⁶⁴⁹ 1.39.^{300a} Ethyl mercaptan and ethyl sulfide are V-shaped molecules.^{300a} The dipole moment has been compared with those of 250 other compounds.⁴⁵⁹ The first ionization potential is 9.7 v.⁵⁹⁷ The viscosity has been measured in several solvents.^{61b} The viscosities of mixtures of ethyl mercaptan and ethanol are slightly below the calculated.¹⁶⁹ Its Raman spectrum has been compared with those of ethyl alcohol and of halides.^{644b} In liquid ammonia sodium ethyl mercaptide has a dissociation constant of about 22.5, which is about six times that of sodium phenate.³⁶⁰ The thermodynamic properties have been thoroughly studied.^{40, 401}

n-Propyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$, m. -113.3°,⁶⁰⁸ -113.80°,¹⁵⁶ -111.5°;⁶¹⁸ b. 67.82°,¹⁵⁶ 67-8°,^{19, 519, 668a} 68-8.5°,^{61a} 67°,^{12, 278c} 67.5°,⁶³² b_{763} 63-7°,^{300b} b_{701} 65.10°;^{412c} $d_{20/4}$ 0.8407,¹⁵⁶ 0.8337°,^{61a} 0.8391,^{300b} $d_{25/4}$ 0.83598;^{412c} $n_{20/D}$ 1.4348,^{300b} 1.4380,^{156, 632} 1.4391,^{61a, 61b} $n_{25/D}$ 1.435,⁶³² 1.43511;^{412c} 3,5-dinitrobenzoate m. 86°.³⁹⁵ The solubility in water at 20° is 0.025 mole or 1.90 g./liter.⁶⁷⁹ The Raman spectra of a number of *n*-propyl and *i*-propyl compounds have been compared.⁴⁹⁷ The critical oxidation potential is 0.812 for *n*-PrSH and 0.819 for *i*-PrSH;¹⁹⁹ the diamagnetic susceptibility is 58.51.¹³¹

i-Propyl, Me_2CHSH , m. -130.63° ,¹⁵⁶ -130.7° ; b. 52.9° ,¹⁸⁴ 56° ,^{278c} $57-60^\circ$,^{19, 128a} $58-9^\circ$; ³⁹⁵ b_{607} 49.90° ,^{412c} d 0/4 0.83559,¹⁸⁴ d 20/4 0.8142,¹⁵⁶ d 25/4 0.80851,¹⁸⁴ 0.80895; ^{412c} n 20/D 1.4256,¹⁵⁶ n 25/D 1.4223,¹⁸⁴ 1.42154; ^{412c} 3,5-dinitrobenzoate m. 86° .³⁹⁵ The lines of the Raman spectra have been determined.^{150a}

n-Butyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, m. -115.9° ,⁶⁰⁸ -116.12° ; b. 98.58° ,¹⁵⁶ b. 98.0° ,¹⁸⁴ 98° ,⁶³² 97° ,¹² $97-8^\circ$,^{11, 19, 61a, 249} $95-7^\circ$,⁸⁰ b_{760} 98.7° ,³²⁵ b_{758} 97.2° ,^{300b} b_{750} $96-8^\circ$,¹⁶⁴ b_{702} 96.10° ; ^{412c} d_0 0.858, d_{18} 0.843,⁵³⁴ d 0/4 0.86006,¹⁸⁴ d 20/4 0.8397,^{300b} 0.8333,^{61a} 0.8408,¹⁵⁶ d 25/4 0.83651,¹⁸⁴ 0.83679; ^{412c} n 20/D 1.4411,^{300b} 1.44402,^{61a, 61b} 1.4426,¹⁵⁶ 1.44074,^{412c} 1.4431,⁶³² 1.4420,¹⁶⁴ 1.442,¹¹ n 25/D 1.4401.¹⁸⁴ The solubility in water at 20° is 0.0066 mole or 0.596 g./liter.⁶⁷⁹ The heat of immersion of silica gel in *n*-butyl mercaptan is 25.9 cal./g., in water 25.4, and in hexane only 7.9.⁵⁸⁶ This mercaptan has been included in a study of Raman spectra.³²⁵ The ionization constant in aqueous *t*-butanol is 11.51.²⁰⁷

i-Butyl, $\text{Me}_2\text{CHCH}_2\text{SH}$, b. 88.72° ,¹⁵⁶ 88° ,^{278c, 299} b_{754} $86.6-7.8^\circ$,⁴⁴⁰ b_{702} 96.10° ; ^{412c} $d_{11.5}$ 0.848,²⁹⁹ d 20/4 0.8350,¹⁵⁶ 0.83573,^{177, 440} d 25/4 0.82880; ^{412c} n 20/D 1.4386,¹⁵⁶ 1.43859,^{177, 440} n 25/D 1.43582.^{412c}

s-Butyl, $\text{CH}_3\text{CH}_2\text{CH}(\text{SH})\text{CH}_3$, m. -165.0° ; ¹⁸⁴ b. 85.15° ,¹⁵⁶ 84.5° ,¹⁸⁴ $84-5^\circ$,⁵¹³ $83-5^\circ$,³³¹ $89-91^\circ$,²⁰⁰ b_{134} 37.4° ; ^{412c} d 0/4 0.84906,¹⁸⁴ d 17/4 0.8289 (d 25/4 0.8211),⁵¹³ d 20/4 0.8294,¹⁵⁶ 0.8290,^{439b} d 25/4 0.82459,¹⁸⁴ 0.82456; ^{412c} n 20/D 1.4367,¹⁵⁶ 1.4365,^{439b} n 25/D 1.4338,¹⁸⁴ 1.43385; ^{412c} l b. $83-4^\circ$; $[\alpha]$ 20/D -11.99° ; ⁴⁰⁸ d b. $85-95^\circ$; $[\alpha]$ 20/D 15.71° ,^{380c} 12.45° .²¹⁵

t-Butyl, Me_3CSH , m. 1.26° ,⁴⁰² 1.11° ,²⁶² 0.82° ,¹⁵⁶ 0° ,^{23, 573} -0.5° ; ⁵¹⁵ b. 64.22° ,⁴⁰² 64.2° ,²⁶² 64.35° ,¹⁵⁶ 63.3° ,^{23, 573} 63° ,⁴⁴² $63.9-4.3^\circ$,³⁵⁰ $65-6^\circ$,¹⁶² $63.7-4.2^\circ$,⁵¹⁵ 64° ,²¹ $63-5^\circ$,³¹⁴ $b_{700.8}$ 61.60° ; ^{412c} d 20/4 0.7999,¹⁵⁶ 0.7981,⁵⁷³ 0.80020,²⁶² d 25/4 0.79472,^{262, 402} 0.79426,^{412c} d 30/4 0.78929; ²⁶² n 15/D 1.4249,^{23, 573} n 18/D 1.4212,⁴⁴² n 20/D 1.4230,¹⁵⁶ 1.4225,⁵⁷³ 1.4231,³¹⁴ 1.4235,⁵⁸¹ 1.42320,²⁶² n 25/D 1.42007,^{262, 402} 1.41984,^{412c} n 30/D 1.41697; ²⁶² viscosity, surface tension and derived functions; ²⁶² solubility in water at 20° 0.0107 mole or 0.964 g./liter.⁶⁷⁹ The thermodynamic properties have been thoroughly investigated from $0^\circ-1000^\circ\text{K}$.⁴⁰²

n-Amyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, m. -75.83° ,²⁰¹ -75.7° ; ^{262, 608} b. 126.64° ,²⁰¹ 126.5° ,^{184, 262} 126° ,^{12, 476} $126-7^\circ$,^{278b} $125-6^\circ$,²⁵ b_{755} 125° ; ^{439b} d 0/4 0.8595,¹⁸⁴ d 20/4 0.8390,^{439b} 0.84209,²⁶² d 25/4

0.8375,¹⁸⁴ 0.83763, d 30/4 0.83317;²⁶² n_D 1.44366,⁴⁷⁶ n 20/D 1.4450,^{439b} 1.44692,²⁶² n 25/D 1.4440,¹⁸⁴ 1.44439, n 30/D 1.44180;²⁶² viscosity, surface tension and derived functions;²⁶² solubility in water at 20° 0.0015 mole or 0.156 g./liter; ⁶⁷⁹ heat of formation 34.65 cal.⁵⁹ Thermodynamic properties have been thoroughly investigated.²⁰¹

i-Amyl, $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{SH}$, b. 117°;³⁶¹ 118–20°;³³⁶ 119.8°;³⁵⁷ 119.5°;⁴⁹ 116.6–8.0°;^{177, 440, 490b} b_{752} 116.5°;⁵³⁸ d_0 0.8548,³⁵⁷ d_{21} 0.835,³⁶¹ d 20/4 0.83475,^{177, 440, 490b} 0.8322;^{439b} n 20/D 1.4420,³³⁶ 1.44118,^{177, 440, 490b} 1.4445;^{439b} dielectric K 4.35 at 22°;⁵³⁸ 4.9 at 18°, 4.4 at 26° and 4.25 at 33°;¹⁷⁸ molecular volume at 0° 121.6;²⁰¹ critical temperature 320.92°.¹⁹⁶

n-2-Methylbutyl, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{SH}$, b. 118–9.5°;^{98, 687} b_{745} 117.4–7.6°;²⁷⁰ 116–7°;^{380g} 119–21°;⁶⁴³ d 25/4 0.8403,^{98, 687} d_{13} 0.848333,²⁷⁰ d_{23} 0.8415;⁶⁴³ $[\alpha]$ 2.20°;^{98, 687} $[\alpha]$ 13/D 2.04°;²⁷⁰ $[\alpha]$ 23/D 3.21°;⁶⁴³ $[\alpha]$ 25/D 2.99°.^{380g}

s-Amyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{SH})\text{CH}_3$, m. –169.0°, b. 112.9°; d 0/4 0.85086, d 25/4 0.82815; n 25/D 1.4386;¹⁸⁴ act. b. 112°; $[\alpha]$ 20/D –4.66°.^{380f}

Pentanethiol-3, $\text{CH}_3\text{CH}_2\text{CH}(\text{SH})\text{CH}_2\text{CH}_3$, b. 105°.^{404a}

t-Amyl, $\text{CH}_3\text{CH}_2\text{CMe}_2\text{SH}$, b. 78°;⁵¹⁴ 97°;²⁰ 97.2–9.4°;³⁵⁰ 98–100°; n 20/D 1.4379.³¹⁴

n-Hexyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, m. –81.03°;⁶⁰⁸ b. 151.5°;¹⁸⁴ 147°;¹² 152–3°;⁹⁶ 145–8°;⁴⁷² 151–2°;²⁵ b_{768} 149°;^{278a, 278b} b_{90} 86.4°;¹⁸⁴ b_{100} 84°;^{170b} d 0/4 0.85911, d 25/4 0.83826,¹⁸⁴ 0.8367,^{170b} d 20/4 0.8526,^{439b} d_{20} 0.8486;^{278a, 278b} n 25/D 1.4473,¹⁸⁴ 1.4460,^{170b} n 20/D 1.4490.^{439b}

s-Hexyl, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{SH})\text{CH}_3$, m. –147.0°; b. 138.9°;¹⁸⁴ 142°;¹⁸⁷ b_{50} 60.6°; d 0/4 0.85217, d 25/4 0.83050; n 25/D 1.4426,¹⁸⁴ 1.4418.⁸⁰

Hexanethiol-3, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{SH})\text{CH}_2\text{CH}_3$, b_{25} 57°; d 20/4 0.831°; n 20/D 1.4428.⁵⁷⁷

2-Mercaptoisohexane, $\text{Me}_2\text{CHCH}_2\text{CH}(\text{SH})\text{Me}$, partially re-cemized $[\alpha]$ 20/D 21.2°.^{380d}

n-Heptyl, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{SH}$, m. –43.4°;⁶⁰⁸ b. 176.2°; b_{30} 81.2°;¹⁸⁴ b. 174–5°;^{668b} 174°;¹² 174–6°;¹ 176–7°;²⁵ b_{49} 90–3°;^{190a} d 0/4 0.85894, d 25/4 0.83891,¹⁸⁴ 0.8399;^{190a} n 25/D 1.4498,¹⁸⁴ 1.4488.^{190a}

s-Heptyl, $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{SH})\text{CH}_3$, m. –141.0°; b. 163.6°; b_{30} 69.6°;¹⁸⁴ b_{765} 164–5°;^{278d, 279} d 0/4 0.85181, d 25/4 0.83114,¹⁸⁴

d_{20} 0.8353; ^{278d}, ²⁷⁹ n 25/D 1.4452,¹⁸⁴ n 20/D 1.44596; ^{278d}, ²⁷⁹ solubility in water at 20° 0.009 g./liter.⁶⁷⁹

Heptanethiol-4, $(CH_3CH_2CH_2)_2CHSH$, b . 135–8°, ^{404a} 157–9°, b_7 40°. ^{339b}

2,4-Dimethylpentanethiol-3, $i\text{-Pr}_2CHSH$, b . 110–3°. ^{404a}

n -Octyl, $CH_3(CH_2)_6CH_2SH$, m . –49.2°; ⁶⁰⁸ b . 199.1°, b_{30} 99.8°, ¹⁸⁴ b . 199–200°, ²⁵ b_{16} 83–4°, ^{170b} 198–200°; ³²⁴ d 0/4 0.85998, d 25/4 0.83956, ¹⁸⁴ 0.8349; ^{170b} n 25/D 1.4519, ¹⁸⁴ 1.4460; ^{170b} ionization constant 11.72.²⁰⁷

s -Octyl, $CH_3(CH_2)_5CH(SH)CH_3$, m . –79.0°; b . 186.4°, ¹⁸⁴ $b_{0.5}$ 69–71°, ¹³⁷ b_{30} 88.9°, ¹⁸⁴ b_{22} 78–80°, ³³¹ b_{23} 85°; ^{170c}, ^{190a} d 0/4 0.85281, ¹⁸⁴ d_{25} 0.9023, ¹³⁷ d 25/4 0.83293, ¹⁸⁴ 0.8314; ^{170c}, ^{190a} n 25/D 1.4481, ¹⁸⁴ 1.4455, ^{170c}, ^{190a} 1.4586; ¹³⁷ $[\alpha]_D$ 9.30°. ^{380b}

i -Octyl, $C_8H_{17}SH$, b_{18} 75°, d 20/4 0.8280; n 20/D 1.45100. ^{61a}, ^{61b}

2-Ethylhexyl, $CH_3CH_2CH_2CH_2CH_2CH_2SH$, b_{19} 80°, ^{190a} b_{35} 90°; ^{190b} d 25/4 0.8467; ^{190a}, ^{190b} n 25/D 1.4524, ^{190b} 1.4541. ^{190a}

t -Octyl, $(CH_3)_3CCH_2C(CH_3)_2SH$, b_{50} 76–7°, ^{175a} 75.5–6.5°; n 20/D 1.4538. ⁵⁸¹

n -Nonyl, $CH_3(CH_2)_7CH_2SH$, m . –20.1°; ⁶⁰⁸ b . 220.2°, ¹⁸⁴ $b_{4.5}$ 75–6°, ²⁵ b_{11} 95–6°, ⁶²¹ b_{30} 117.4°, ¹⁸⁴ b_{20} 100–4°; ⁴⁵⁰ d 0/4 0.85907, d 25/4 0.84015, ¹⁸⁴ d 20/4 0.8371, ⁴⁵⁰ 0.8425; ⁶²¹ n 20/D 1.45197, ⁴⁵⁰ 1.4560, ⁶⁴¹ n 25/D 1.4537. ¹⁸⁴

s -Nonyl, $CH_3(CH_2)_6CH(SH)CH_3$, m . –69.0°; b . 208.2°, b_{30} 106.8°; d 0/4 0.85313, d 25/4 0.83384; n 25/D 1.4500. ¹⁸⁴

Nonanethiol-5, Bu_2CHSH , b_7 72°. ^{339b}

2,6-Dimethylheptanethiol-4, $i\text{-Bu}_2CHSH$, b . 155–8°. ^{404a}

n -Decyl, $CH_3(CH_2)_8CH_2SH$, b_2 96°, ⁶²¹ b_5 96–7°, ²⁵ b_{13} 114–5°, ⁹⁶ b_{19} 125–7°, $b_{21.5}$ 126.5–6.8°; ⁵⁷⁰ d 20/4 0.8395, ⁴⁵⁰ 0.8414; ⁶²¹ n 20/D 1.45367, ⁴⁵⁰ 1.4576, ⁶²¹ 1.4569. ⁵⁷⁰

n -Undecyl, $CH_3(CH_2)_9CH_2SH$, b_3 103–4°, ²⁵ b_{20} 139.9–40.0°, ⁵⁷⁰ b_{21} 138–41°; d 20/4 0.8417; n 20/D 1.45816, ⁴⁵⁰ 1.4588. ⁵⁷⁰

n -Dodecyl, Lauryl, $CH_3(CH_2)_{10}CH_2SH$, m . 18–20°; ¹³⁵ $b_{1-1.5}$ 95–6°, ⁶⁰⁵ b_3 111–2°, ²⁵ b_5 124°, ³⁶⁷ $b_{6.5}$ 114–6°, ³⁵³ b_{15} 142–5°, ¹⁷⁹, ¹⁸², ^{276b} $b_{20.5}$ 153.7–3.9°, ⁵⁷⁰ b_{24} 153–5°, ⁴⁵⁰ b_{26} 155°, ^{170b} b_{39} 165–9°; ⁶³⁰ d 20/4 0.8435, ⁴⁵⁰ d 25/4 0.8411; n 25/D 1.4558, ^{170b} n 20/D 1.45886, ⁴⁵⁰ 1.4589. ²¹⁴, ³⁵³, ⁵⁷⁰

4-Butyloctanethiol-1, $Bu_2CHCH_2CH_2CH_2SH$, $b_{2.5}$ 98–9°; d 20/4 0.858; n 20/D 1.4625. ²¹⁴

Dodecanethiol-6, $CH_3CH_2CH_2CH_2CH_2CH(SH)CH_2CH_2CH_2CH_2CH_2CH_3$, b_{10} 129°; d 20/4 0.857; n 20/D 1.4566. ²¹⁴

5-Propylnonanethiol-5, Bu_2PrCSH , $b_{2.5}$ 84° ; d 20/4 0.860; n 20/D 1.4633.²¹⁴

2-Methylundecanethiol-2, $\text{Me}_2\text{C}(\text{SH})\text{C}_9\text{H}_{20}$, $b_{1.3}$ $73-5^\circ$; d 20/4 0.853; n 20/D 1.4558.²¹⁴

t-Dodecyl, $\text{C}_{12}\text{H}_{25}\text{SH}$ (from triisobutylene), b . $227-8^\circ$.⁵²

n-Tridecyl, $\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{SH}$, b_{22} $162-6^\circ$,⁴⁵⁰ $169.6-71.7^\circ$; ⁵⁷⁰ d 20/4 0.8453; n 20/D 1.45906,⁴⁵⁰ 1.4595.⁵⁷⁰

n-Tetradecyl, myristyl, $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2\text{SH}$, m . 7° ; b_{20} $179.8-80.9^\circ$; ⁵⁷⁰ b_{22} $176-80^\circ$; d 20/4 0.8469; n 20/D 1.46005,⁴⁵⁰ 1.4607.⁵⁷⁰

n-Pentadecanethiol-8, $(\text{C}_7\text{H}_{13})_2\text{CHSH}$, m . -10.5° ; b_{10} $158-60^\circ$; n 25/D 1.4580.^{170c}, ^{190a}

Cetyl, $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{SH}$, m . 19° ,²² 18° ,³¹, ²⁰⁶, ⁶⁷⁴ 52° *,¹³⁵ 50.5° *; ²²¹ $b_{0.5}$ $123-8^\circ$,²⁰⁶ b_1 150° ,^{170b} b_5 $173-5^\circ$, b_{10} $187-9^\circ$,²² $b_{0.6}$ $135-40^\circ$; ⁶⁷⁴ magnetic susceptibility -390.4 .¹⁴³

n-Heptadecanethiol-7, $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{SH})(\text{CH}_2)_9\text{CH}_3$, b_1 153° ; d 25/4 0.8384; n 25/D 1.4594.^{170c}

n-Heptadecanethiol-9, $(\text{C}_8\text{H}_{17})_2\text{CHSH}$, b_{18} $196-7^\circ$.^{190a}

n-Octadecyl, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2\text{SH}$, m . 56° *,¹³⁵ 32.5° .⁵⁵⁷

Melissyl, $\text{CH}_3(\text{CH}_2)_{28}\text{CH}_2\text{SH}$, m . 94.5° .⁴⁷⁷

Allyl, $\text{CH}_2:\text{CH}:\text{CH}_2\text{SH}$, b . 90° ,¹⁰⁹, ¹⁵⁵, ²⁸⁸ $63-6^\circ$,⁴⁹³ $66-7^\circ$,²¹ $67-9^\circ$,²² $67-8^\circ$; d 23/4 0.9250,⁹⁴ d 20/4 0.9304; n 20/D 1.4680;⁴⁹³ 3,5-dinitrobenzoate, m . 52° .³⁹⁵

Crotyl, 2-butenethiol-1, $\text{CH}_3:\text{CH}:\text{CH}:\text{CH}_2\text{SH}$, b . $99-101^\circ$; d 23/4 0.8830.⁹⁵

1-Butenethiol-4, $\text{CH}_2:\text{CH}:\text{CH}_2:\text{CH}_2\text{SH}$, b . $98-103^\circ$; d 22/4 0.9087.⁹⁵

Methallyl, *i*-butenyl mercaptan, *i*-butenethiol-3, b . 93.5° ,²² b . 92.5° ; d 20/4 0.9137; n 20/D 1.4872.⁶⁰⁴

1-Pentenyl, 1-pentenethiol-5, $\text{CH}_2:\text{CH}:\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, b . $135-7^\circ$; d 18.5/4 1.0748.⁹⁵

2-*i*-Pentenyl, 2-*i*-pentenethiol-4, $(\text{CH}_3)_2\text{C}:\text{CH}:\text{CH}_2\text{SH}$, b . $125-7^\circ$; d 18/4 0.8987.⁹⁵

Oleyl, $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{CH}_2\text{SH}$, $b_{0.05}$ $171-5^\circ$, $b_{0.2}$ $171-8^\circ$; n 20/D 1.4669, n 17/D 1.4712.^{375a}

Cyclopentyl, $(\text{CH}_2\text{CH}_2)_2\text{CHSH}$, b . $131.5-2^\circ$,³⁹¹ 130° ,⁶²⁰ $130-2.4^\circ$,³⁵¹ $129.5-30.5^\circ$; ⁶¹⁹ d 20/4 0.9485,⁶²⁰ 0.9551; ⁶¹⁹ n 20/D 1.4882,⁶²⁰ 1.4871.⁶¹⁹

Cyclohexyl, $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{CHSH}$, b . $158-60^\circ$,^{83a} 155° ,^{528b} b_{755} $150-2^\circ$,⁴⁰⁵ b_{763} 157° ,¹⁴⁶ b_{757} 156° ,¹⁴⁶ $157-62^\circ$,³³⁴ $158-60^\circ$,^{83a}

* Probably disulfide.

155–65°, ⁵⁷⁵ 162–5°, ⁵⁸² b_{12} 41°, ⁴⁴² b_{100} 90°, ^{170c}, ^{190a}, ^{190b}, ⁶⁰⁵, ⁶²⁰ 88–9°, ⁶¹⁹ b_{64} 93–7°, ⁶⁸¹ b_{19} 51–4°; ⁶⁵² d_0 0.9905, d_{20} 0.9782, ⁴⁰⁵ d 20/4 0.9525, ⁶¹⁹ 0.9584, ⁶²⁰ 0.9486; ^{170c}, ^{190a} n_D 1.481, ⁴⁰⁵ n 18/D 1.4988, ⁴⁴² n 20/D 1.4933, ^{170c}, ^{190a}, ⁶⁵² 1.4910, ⁶¹⁹ 1.4911, ⁶²⁰ n 25/D 1.4738, ⁵⁷⁵

Cyclopentylmethyl, $C_5H_9CH_2SH$, b . 170°; ⁴³³, ⁴³⁴ d_{25} 0.91, ⁴³³ d_{25} 0.938; ⁴³⁴ n 25/D 1.4770. ⁴³³, ⁴³⁴

Cycloheptyl, $(\cdot CH_2CH_2CH_2)_2 CHSH$, b_{11} 74°. ³⁹¹

3-Methylcyclopentylmethyl, $MeC_5H_8CH_2SH$, b . 180°; d_{25} 0.928; n 25/D 1.4675. ⁴³³, ⁴³⁴

2-Methylcyclohexyl, m . 0°; ⁴⁴² b . 161°, ^{528b} 165°, ¹⁴⁶ b_{14} 56°. ⁴⁴²

3-Methylcyclohexyl, b . 172–4°, ^{83b} 168°, ^{528b} 145°, b_{30} 80–2°. ⁶⁸¹

cis-3-Methylcyclohexyl, b . 165°; d_{25} 0.916; n 25/D 1.4647; ⁴³³. ⁴³⁴ $[\alpha]_{546}$ –2.74°. ⁴³³

trans-3-Methylcyclohexyl, b . 171°; d_{25} 0.9140; n 25/D 1.4663; ⁴³³, ⁴³⁴ $[\alpha]_{546}$ 5.50°. ⁴³³

4-Methylcyclohexyl, b . 169°. ^{528b}

3-Methylcyclohexylmethyl, $CH_3C_6H_{10}CH_2SH$, b . 190°; ⁴³³, ⁴³⁴ d_{25} 0.9350; ⁴³⁴ 0.932; ⁴³³ n 25/D 1.4720. ⁴³³, ⁴³⁴

β -Tetrahydronaphthyl, b_{15} 151–1.5°; d 20/4 1.0884; n 20/D 1.5972. ⁶²⁰

β -Decahydronaphthyl, b_{20} 122°, ⁴³³ b_{25} 122°; ⁴³⁴ d_{25} 0.980, ⁴³³ d_{20} 0.9950; ⁴³⁴ n 25/D 1.5110. ⁴³³, ⁴³⁴

1-Cyclopentenyl, C_5H_7SH , b . 116°; d 19.5/4 0.8947. ⁹⁵

2-Cyclohexenyl, C_6H_9SH , b . 156°; d_{25} 0.953; n 25/D 1.4686. ⁴³⁴

β -Cyclohexylethyl, $C_6H_{11}CH_2CH_2SH$, b_1 50–2.5°; n 25/D 1.4910. ¹²⁹

2,2,6,6-Tetramethylcyclohexyl, $Me_4C_6H_7SH$, m . 36°; b_7 81–2°. ³⁶³

ϵ -Cyclohexylamyl, $C_6H_{11}CH_2CH_2CH_2CH_2CH_2SH$, b_1 89.5–91°; n 25/D 1.4820. ¹²⁹

δ -(β -Tetrahydronaphthyl)butyl, $C_{10}H_{11}CH_2CH_2CH_2CH_2SH$, b_1 143°; n 25/D 1.5569. ¹²⁹

δ -(β -Decahydronaphthyl)butyl, $C_{10}H_{17}CH_2CH_2CH_2CH_2SH$, $b_{0.5}$ 124°; n 25/D 1.5092. ¹²⁹

Cholesteryl, $C_{27}H_{45}SH$, m . 99.5°; ⁵⁹³, ⁶⁴⁵ $[\alpha]_D$ –23.85°. ⁶⁴⁵

Furfuryl, $C_4H_3OCH_2SH$, b . 155°, ²⁴³ b_{65} 84°; ²⁴³, ³⁴² d 20/4 1.13186; n 20/D 1.5329. ³⁴²

5-Methylfurfuryl, $MeC_4H_2OCH_2SH$, b_3 70°; n 20/D 1.5258. ³⁴⁰

2-Thiophenethiol, $C_4H_3S\cdot SH$, b . 171.1°, ¹⁰⁷ 166°, ⁴²³ b_{15} 86°; d 19.5/4 1.168; n 15/D 1.5750, ¹⁰⁸ n 20/D 1.6201; ¹⁰⁷ $Ac.$, b . 230–2°. ⁴²³

3-Thiophenethiol, $C_4H_3S \cdot SH$, b. 171° ; d 25/4 1.247; n 20/D 1.6157.¹⁰⁰

2-Ethyl-3-thiophenethiol, b. $195-7^\circ$.¹¹⁶

Trimethylsilyl, Me_3SiSH , b. $77-8^\circ$.¹¹⁹

Dimercaptans

gem-Dithiols, $RCH(SH)_2$ and $R_2C(SH)_2$ ¹¹⁰

$H_2C(SH)_2$, b_{80} 58° ; n 25/D 1.5840; diBz., m. 119.5°

EtCH(SH)₂, b. 142° , b_{42} 60° ; d 25/4 1.043; n 25/D 1.5214; diAc., $b_{0.4}$ $61-2^\circ$; n 25/D 1.5150.

$MeCMe_2CH_2CHMeCH_2CH(SH)_2$, $b_{0.5}$ $60-3^\circ$; d 25/4 0.935; n 25/D 1.4875; diAc., $b_{0.2}$ $96-100^\circ$; n 25/D 1.4930.

$Me_2C(SH)_2$, m. $4-8^\circ$; b. $113-6^\circ$, b_{105} $61-2^\circ$; d 25/4 1.006; n 25/D 1.5063.

Et₂C(SH)₂, b_{47} $80-2^\circ$; n 25/D 1.5042.

$H_2C(CH_2CH_2)_2C(SH)_2$, b_8 $69-73^\circ$; d 25/4 1.083; n 25/D 1.5440.

PhCH(SH)₂, $b_{0.9}$ $74-6^\circ$; n 25/D 1.6218; diAc., m. 38° ; $b_{0.5}$ 122° ; n 25/D 1.580°; diBz., m. 138° .

TABLE 16.1

*Some Properties of α,ω -Dimercaptans*²⁶⁶

No.	m.p. °C	b_{10} °C	b_{100} °C	b_{760} °C	$d^\circ/4$	$d^{25}/4$	n^{25}/D	Latent Heat of Vaporization
2	-41.2 ⁶²⁷	—	—	146.0	1.1454	1.1192	1.5558 ⁶²⁷	—
3	-79.0 ⁴¹⁷	—	104.6	172.9	1.1007	1.0775	1.5371	—
4	-53.9	74.5	127.7	195.6	1.0621	1.0395	1.5265	11,135
5	-72.5	90.1	147.2	217.3	1.0375	1.0158	1.5194	11,842
6	-21.0	106.0	163.8	237.1	1.0102	0.9886	1.5077	12,246
7	-38.1	119.5	178.0	252.2	0.9900	0.9707	1.4950	12,845
8	0.9	132.0	192.4	269.3	0.9814	0.9620	1.5009	13,217
9	-17.5	145.0	206.5	284.0	0.9698	0.9510	1.4940	13,897
10	17.8	161.0	219.5	297.1	—	0.9432	1.4950	14,590
11	-5.4	171.5	230.6	308.8	—	0.9368	1.4931	15,090
12	28.4	181.5	241.0	319.3 *	—	0.9270 †	—	15,660

* Extrapolated.

† $d^{30}/4$.

The boiling points at 10 mm. are from distillations, those at 100 and 760 mm. were taken with the Cottrell apparatus.

The dimercaptans are weak acids; their normal acidity potentials at 20° in alcoholic solution in volts are in the Table 17.1.

TABLE 17.1

Acidity Potentials of the Dimercaptans, HS(CH₂)_nSH ⁵⁴⁹

Alcohol Volume %	n = 2		3		4		5	
	H ₂ X	HX'	H ₂ X	HX'	H ₂ X	HX'	H ₂ X	HX'
95.0	-0.6758	—	-0.7055	—	-0.7413	—	-0.7528	—
78.0	-0.6487	—	-0.6734	(-0.812)	-0.7031	(-0.826)	-0.7119	(-0.808)
60.0	-0.6248	(-0.811)	-0.6474	-0.769	-0.6680	-0.770	-0.6869	-0.771
42.3	-0.5958	(-0.789)	-0.6137	-0.703	-0.6355	-0.726	-0.6486	-0.720

Properties of Some Dimercaptans

Ethylene, ethanedithiol-1,2, HSCH₂CH₂SH, m. -41.0°; b. 146-6.5°, ²⁶⁶, ⁶²⁷ 146°, ⁸, ¹⁹, ¹⁵⁵, ⁴²², ^{646b}, ⁶⁵⁴ b₁₄ 43-4°, b₁₆ 46-7°, ⁵⁶⁶ b₆₀ 67°, ³⁶⁸ b₂₅ 53-5°, ^{191a} b₂₆ 54.2°, ^{412a} b₇₂₀ 140-1°; ⁵⁴⁹ d 20/4 1.122, ⁵⁶⁶ 1.1243, ^{412a} d_{23.5} 1.123, ⁶⁵⁴ d 23/4 1.123, ¹⁹ d 25/4 1.1185; n 20/D 1.5590, ^{412a} n 25/D 1.5558; ²⁶⁶, ⁶²⁷ diAc. m. 60°, ⁵⁰³ 69°; diBz. m. 95°. ^{412a}

Trimethylene, HSCH₂CH₂CH₂SH, m. -79°; ⁴¹⁷ b. 172.9°, ²⁶⁶ 169°, ²⁶⁰, ⁶²⁷ 169-70°, ¹⁷ 170-1°, ⁶⁸² b₇₂₀ 160-1°, ⁵⁴⁹ b₁₅ 63°, ^{412a} b₆₀ 94°, ⁵⁶⁶ b₁₂₀ 110°, ¹²⁰ b₁₀₀ 104.6°; ²⁶⁶ d 0/4 1.1007, d 25/4 1.0775, d 20/4 1.0772, ⁶⁸² 1.0783; ^{412a} n 20/D 1.5392, ⁶⁸² 1.5406, ^{412a} n 25/D 1.5371; ²⁶⁶ diAc., b₂₄ 152°, ¹²⁰ b₁ 104-5°; d 20/4 1.1401; n 20/D 1.5406, ^{412a} n 24/D 1.5209; ¹²⁰ diBz., m. 56.3°. ^{412a}

Propanedithiol-1,2, CH₃CH(SH)CH₂SH, b. 152°, ¹⁹, ⁴⁷⁴, ⁴⁸⁹ b₁₇ 51-2°, ⁵⁶⁶ b₅₅ 72-4°; ¹⁴⁵ d 20/4 1.061. ⁵⁶⁶

Tetramethylene, HSCH₂CH₂CH₂CH₂SH, m. -53.9°; b. 195.6°, ²⁶⁶ b₃₀ 105-6°, ^{91a} b₁₁ 75-6°; ⁵⁴⁹ diBz., m. 49°, ^{91a} 49.5°. ⁵⁴⁹

Butanedithiol-2,3, CH₃CH(SH)CH(SH)CH₃, b₅₀ 86-7°. ³⁶⁸

Pentamethylene, HSCH₂CH₂CH₂CH₂CH₂SH, m. -72.5°; b. 217.3°, ²⁶⁶ b₁₅ 108-9°, b₂₇ 123°, ¹⁵ b₁₅ 107-8°, ⁵⁴⁹ b₁₆ 110°; ^{91a} diBz., m. 45°. ¹⁵, ^{91a}

2,2-Dimethylpropanedithiol-1,3, HSCH₂C(CH₃)₂CH₂SH, b₁₂ 72°. ²⁴

Hexamethylene, HSCH₂CH₂CH₂CH₂CH₂CH₂SH, m. -21.0°; b. 237.1°, ²⁶⁶ b₁₅ 118-9°; diBz., m. 57°. ^{91a}

Hexanedithiol-1,2, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, b_{14} 99° ; n 19/D 1.5071.²⁶

Decamethylene, $\text{HSCH}_2(\text{CH}_2)_8\text{CH}_2\text{SH}$, m . 17.8° ,²⁶⁶ 20° ; ^{91a}
 b . 297.1° ,²⁶⁶ b_{16} 176° ,^{91a} b_9 $99-102^\circ$; ^{170b} diBz. , m . 55° .^{91a}

2,6-Dimethyloctanedithiol-3,7, b_{11} 132° ; n 17/D 1.5025.⁴⁴²

2,6-Dimethyloctanedithiol-2,6, b_9 110° ; n 16/D 1.4971.⁴⁴²

Pentadecanedithiol-7,8, $\text{C}_6\text{H}_{13}\text{CH}(\text{SH})\text{CH}(\text{SH})\text{C}_7\text{H}_{15}$, b_{16} $196-7^\circ$.³⁶⁸

Octadecamethylene, $\text{HSCH}_2(\text{CH}_2)_{16}\text{CH}_2\text{SH}$, m . 52° .²⁶⁶

Cyclohexanedithiol-1,2, $\text{C}_6\text{H}_{10}(\text{SH})_2$, b_{15} 97° .¹⁴⁵

1,1-bis (mercaptomethyl) cyclohexane, $\text{C}_6\text{H}_{10}(\text{CH}_2\text{SH})_2$, b_{17} 136° .²⁴

3,4-Thiophenedithiol, $\text{C}_4\text{H}_2\text{S}(\text{SH})_2$, b_2 $120-5^\circ$; d 25/4 1.446; n 20/D 1.70.³⁹⁷

Propanetrithiol-1,2,3, trithioglycerol, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.4}$ 60° ,⁵⁶⁶ b_2 80° ,⁴²⁶ b_{15} $115-20^\circ$; ^{516, 609} d 20/4 1.231; ⁵⁶⁶ n 22/D 1.6105.⁴²⁶

Neopentane-tetrathiol, $\text{C}(\text{CH}_2\text{SH})_4$, m . 73° .^{190b}

Properties of Some Aromatic Mercaptans

Thiophenol, $\text{C}_6\text{H}_5\text{SH}$, m . -14.9° ; ⁴⁶⁶ b . 169.5° ,^{85, 87, 138} 168.3° ,⁶⁷⁶ 168° ,^{377, 677} 165° ,⁶³⁹ 172.5° ,^{6, 155} b_{743} $168-9^\circ$,²⁰³ b_{750} $168-70^\circ$,^{603d} b_{50} 86.2° ,⁸⁵ 84° ,³⁶⁷ b_{100} 103.6° ,⁸⁵ b_{30} 77° ,¹⁸⁰ b_{20} 68° ,²⁴² b_{22} 68° ; ⁶²⁰ d 20/4 1.0780, ⁶²⁰ d 23.2/4 1.0739,^{87, 180} d 24/4 1.078,^{155, 639} d 25/4 1.0728; ⁶⁴⁷ n 14/D 1.5931,^{603d} n 20/D 1.587,^{11, 87} 1.5888,⁶²⁰ 1.5855,²⁴² n 23/D 1.55613,¹⁸⁰ n 25/D 1.5805;¹⁹⁸ heat of fusion 24.90 cal./g.; specific heat at 25° 0.3829; entropy at 25° 52.6 ⁴⁶⁶ viscosity, surface tension and parachor.⁶³⁶

o-Thiocresol, $\text{CH}_3\text{C}_6\text{H}_4\text{SH}$, m . 15° ; ^{85, 296, 377} b . 194.3° ,⁸⁵ $187-8^\circ$,³⁷⁷ b_{50} 106° , b_{100} 124.7° .⁸⁵

m-Thiocresol, b . 195.4° ,⁸⁵ 195° ,^{78, 606} b_{25} $90-3^\circ$, b_{50} 107° ,⁶⁰⁶ b_{50} 107.5° , b_{100} 126° ; ⁸⁵ *p*-nitrobenzoate m . 96° .³⁵

p-Thiocresol, m . 43.5° ,¹⁹⁸ 43° ,^{294, 318, 367, 377, 494, 603d} $43-4^\circ$; ²⁰³ b . 195° ,⁸⁵ 194° ,^{122, 631} $190-2^\circ$,¹⁴⁰ $187-8^\circ$,³⁷⁷ b_{100} 124.9° .⁸⁵

o-Ethylthiophenol, b_{730} $207-9^\circ$,²⁶⁷ b_{768} $210.1-0.9^\circ$; d 20/4 1.0349; n 20/D 1.56995.²²⁰

p-Ethylthiophenol, b_{12-3} $91-3^\circ$.⁴⁸³

2,4-Thioxymol, b . $207-8^\circ$.²³³

2,5-Thioxymol, b . $205-6^\circ$.²³³

o-Propylthiophenol, b_{730} $219-21^\circ$.²⁶⁷

- o*-*i*-Propylthiophenol, b_{730} 225–7°. ²⁸⁷
p-*i*-Propylthiophenol, b_{14} 100–4.5°; d 20/4 1.0009; n 20/D 1.5542. ²⁴¹
o-Allylthiophenol, $C_3H_5C_6H_4SH$, b_{17} 183–90°; n 21/D 1.6098. ³⁰²
2-Allyl-4-methylthiophenol, $Me(C_3H_5)C_6H_2SH$, b_{11} 190–6°; n 21/D 1.6921. ³⁰²
o-Phenylthiophenol, $C_6H_5C_6H_4SH$, b_{12} 160°. ⁹²
p-Phenylthiophenol, $C_6H_5C_6H_4SH$, m . 111°. ²³¹
o-Chlorothiophenol, b . 204–6°, ¹⁴⁸ 205–6°; ²²³ $d_{19.5}$ 1.2752. ¹⁴⁸
m-Chlorothiophenol, b . 205–7°; $d_{12.5}$ 1.2637. ¹⁴⁸
p-Chlorothiophenol, m . 54°; ¹⁴⁸, ⁴⁶¹, ^{603d} b . 205–7°. ¹⁴⁸
2,5-Dichlorothiophenol, b_{50} 112–6°. ²³⁵
o-Chloro-*p*-phenylthiophenol, m . 196°. ²⁴⁴
o-Bromothiophenol, b_{11} 96.5°, ⁵⁴⁸ b_{18} 117–8°; n 24/D 1.6321. ⁶⁶⁵
m-Bromothiophenol, b_{20-2} 119–21°, ⁶⁶⁵ b_{40} 123–4°; ⁷⁹ n 20/D 1.6338, ⁷⁹ n 25/D 1.6310. ⁶⁶⁵
p-Bromothiophenol, m . 75°, ⁴⁵, ⁸⁶, ²⁸⁰, ²⁹⁵ 71°; ^{603c}, ^{603d} b . 230–1°; ⁴⁵ Ac . m . 52°; Bz . m . 84.5°. ⁶⁶⁵
o-Iodothiophenol, b_{11} 119.5°. ⁵⁴⁸
m-Iodothiophenol, b_{11} 121.3°. ⁵⁴⁸
p-Iodothiophenol, m . 85°, ⁶⁹⁰ 86°. ⁴⁶
o-Nitrothiophenol, m . 61°, ⁴²⁷ 58°, ³⁷³ 56°, ⁴²⁰ 45°. ⁷⁴
m-Nitrothiophenol, oil . ⁷⁹, ³⁷²
p-Nitrothiophenol, m . 77°. ²²⁸, ^{661b}
2,4-Dinitrothiophenol, m . 132°, ²⁴⁶ 131°; ^{661a} Bz . m . 113°. ^{661b}
2,4,6-Trinitrothiophenol, m . 114°. ^{661a}
2,4-Nitrobromothiophenol, m . 110°. ⁷⁴
2,4-Nitrochlorothiophenol, m . 122°, ⁷⁴ 120°, ²⁸⁶ 213°. ⁵⁰
2,5-Nitrochlorothiophenol, m . 171°. ⁵⁰
m-Methylsulfonylthiophenol, m . 69°. ⁶²⁹
p-Methylsulfonylthiophenol, m . 68°. ⁷⁹
Benzyl, b . 195°, ¹, ^{170c}, ^{190a} 194–5°, ²²⁶ b_3 64.5–5.5°, ⁵¹⁸ b_{22} 100°, ¹²⁰ b_{32} 99°; d 25/4 0.8097; n 20/D 1.5779, ^{170c}, ^{190a} 1.576. ¹¹
o-Nitrobenzyl, m . 29.5°; b_{15} 149.5°. ^{490a}
m-Nitrobenzyl, m . 12°, ³⁹⁸ 14°; b_{18} 164°. ^{490a}
p-Nitrobenzyl, m . 52.5°. ^{490a}
 α -Phenylethyl, b . 119–20°, ⁴⁴ b_{15} 87–8°, ^{289b} b_{10} 81–3°, ^{289c} b_{14} 83–4°; d 18/4 1.0396, ⁴⁶⁴, ⁵⁷⁴ d 20/4 1.022; ^{289c} n 18/D 1.5691, ⁵⁷⁴ n 20/D 1.557; $[\alpha]$ 26/D 105.6°, –105.6°; ^{289c} Ac ., b_{13} 123–5°; d 20/4 1.0698; n 20/D 1.5480. ^{289b}

β -Phenylethyl, b_{17} 104° ,^{339a} b_{15} $96-8^\circ$,⁴⁶⁴ b_{14} $96-7^\circ$,^{289b} b_{23} 105° ; ^{91b} d $18/4$ 1.0318 ; n $19/D$ 1.5643 ; ⁵⁷⁴ Ac., b_{13} $134-5^\circ$; d $20/4$ 1.0730 ; n $20/D$ 1.5478 .^{289b}

α -Phenylpropyl, b_{15} $103-4^\circ$.^{380e}

γ -Phenylpropyl, b_{10} 109° ,^{91b} b_{23} $120-2^\circ$; ⁴⁶⁴, ⁵⁷⁴ d $17/4$ 1.010 ,⁴⁶⁴ 1.0107 ; ⁵⁷⁴ n $19/D$ 1.5492 ,⁴⁶⁴ 1.5543 .⁵⁷⁴

β -Phenylpropyl, b_1 74° ; n $20/D$ 1.5510 ; Ac., b_4 105° ; n $20/D$ 1.5429 ; ¹⁰³ d b_{15} $70-1^\circ$; $[\alpha]$ $25/D$ 93° .³⁸¹

β -Phenyl-*i*-propyl, b_{16} $105-10^\circ$; d $19/4$ 0.999 ; n $20/D$ 1.5312 .³³¹

α - β -Phenylbutyl, $b_{1.3}$ 81° ; $[\alpha]$ $25/D$ 7.0° .³⁸¹

ϵ -Phenylamyl, b_{10} $132-4^\circ$.^{91b}

α,β -Diphenylethyl, b_4 $146-8^\circ$.²⁷⁴

o-Methylbenzyl, b_5 $57-8^\circ$; n $25/D$ 1.5702 .²⁷⁴

m-Methylbenzyl, b_{12} 90° .⁹³

p-Methylbenzyl, b_{11} $89-90^\circ$,⁹³ b_{35} 118° .³⁸⁵

2-Nitro-*p*-tolyl, m . 58° .²⁸⁰

α -(*o*-Tolyl) benzyl, b_4 $149-50^\circ$.²⁷⁴

α -(*p*-Tolyl) benzyl, b_8 $159-62^\circ$.²²⁹

o-Chlorobenzyl, b_{25} $120-1^\circ$,⁷⁷ b_{28} $126-8^\circ$; n $25/D$ 1.5840 ,³⁸⁵ 1.5650 .⁷⁷

m-Chlorobenzyl, b_{19} $120-1^\circ$; n $25/D$ 1.5810 .³⁸⁵

p-Chlorobenzyl, m . 85° ; ³¹⁶ $b_{0.4}$ $66-7^\circ$.³⁸⁵

2,4-Dichlorobenzyl, b_{29} $151-2^\circ$; n $29/D$ 1.5993 .⁷⁷

3,4-Dichlorobenzyl, $b_{0.5}$ $87-90^\circ$,³⁸⁵ b_{31} $170-1^\circ$; n $29/D$ 1.6003 .⁷⁷

p-Bromobenzyl, $\text{BrC}_6\text{H}_4\text{CH}_2\text{SH}$, m . 75° .³¹⁵

α -Phenyl-*p*-chlorobenzyl, *p*- $\text{ClC}_6\text{H}_4\text{CHPhSH}$, $b_{5.8}$ $168-9^\circ$.²²⁹

3-Hydroxy-5-methoxybenzyl, $b_{0.08}$ $75-80^\circ$; n $20/D$ 1.5940 .³⁴⁰

Cinnamyl, $\text{C}_6\text{H}_5\text{CH}:\text{CHCH}_2\text{SH}$, m . $7-8^\circ$; b_{13} $124-5^\circ$,⁹⁴ $b_{0.1}$ $116-8^\circ$; ^{375a} 3,5-dinitrobenzoate m . 115° .³⁹⁵

β,γ -Diphenylallyl, $b_{0.01}$ $105-6^\circ$; 3,5-dinitrobenzoate m . 157° .³⁹⁵

4,4'-Dichlorobenzhydryl, $b_{5.8}$ $168-9^\circ$.²²⁹

Triphenylmethyl, Ph_3CSH , m . 107° ; ³³, ³³⁵, ⁶⁴¹ Ac., m . $139-41^\circ$; Bz., m . 185° .⁶⁴¹

α -Thionaphthol, b . 285° ,^{603d} b_{200} 208.5° , b_{50} 187.2° , b_{20} 161° ,³⁵⁸ b_2 $138-40^\circ$, b_7 $142-2.5^\circ$,⁶²⁰ b_{15} $152.5-3.5^\circ$; d $0/4$ 1.1729 , d $23/4$ 1.1549 ,³⁵⁸ d $20/4$ 1.607 ; n $20/D$ 1.6802 ; ⁶²⁰ Bz., m . 118° .^{603a}

β -Thionaphthol, m . 81° ; ³⁵⁸ b . 286° ,⁸⁵ b_{100} 210.5° , b_{50} 189° , b_{20} 162.7° , b_{15} 153.5° ,³⁵⁸ b_{15} $153-4^\circ$.⁶⁸⁸

- 4-Chloro- α -thionaphthol, m. 44° .^{603d}
 4-Bromo- α -thionaphthol, m. 56° .^{603d}
 2-Nitro- α -thionaphthol, m. $70-3^\circ$,³⁹⁶ 205° ; Ac., m. 103° .²⁸⁵
 4-Nitro- α -thionaphthol, m. $77-9^\circ$.³⁹⁶
 5-Nitro- α -thionaphthol, Ac., m. 182° .²⁸⁵
 1-Nitro- β -thionaphthol, m. $98-100^\circ$.³⁹⁶

Some Selenomercaptans

- Phenyl selenomercaptan, b. 182° .^{603c}
 o-Selenocresol, b₂₅ 99° .²⁰⁹
 m-Selenocresol, b₁₆ 89° .²⁰⁹
 p-Selenocresol, m. 47° .^{603c}
 p-Bromoselenophenol, m. 77° .^{603c}
 p-Chloroselenophenol, m. 55° .^{603c}
 α -Selenonaphthol, b₂₀ 167° .^{603c}

TABLE 18.1

*Acidity Constants of Some Substituted Thiophenols in 48%
Ethanol at 25°* ⁷⁰

Substituent	pKa	Substituent	pKa	Substituent	pKa
p-HO	8.30	p-Br	6.99	m-Cl	6.74
p-Me	8.03	p-Cl	6.96	m-NO ₂	5.90
p-MeO	7.99	p-I	6.94	m-MeSO ₂	5.88
m-Me	7.96	m-I	6.82	p-MeSO ₂	5.57
H	7.76 *	m-Br	6.77	p-NO ₂	5.11
m-MeO	7.45				

* PhSH 8.05.⁵²¹

Aromatic Dimercaptans

Dithio-catechol, o-C₆H₇(SH)₂, m. 28° ; ⁴⁸² b. $238-9^\circ$,²⁵⁷ b₁₇ $119-20^\circ$; diAc., m. 88.5° .⁴⁸²

Dithioresorcinol, m-C₆H₄(SH)₂, m. 27.1° ,³⁴⁸ 27° ,⁴⁷¹ 25° ; ²⁰²,⁴⁸³, ⁶⁹¹ b. 245° ,²⁰² 243° ,⁸⁵ b₁₇ 123° ,²⁰², ⁶⁹¹ b₂₈ 141° ,²⁰² b₂₀ 132° ,
b₁₀₀ 176.5° .⁸⁵

Dithiohydroquinone, m. 98° .³⁴⁸, ^{411b}, ⁴⁶⁵, ⁶⁸⁹

4,5-Dimethyldithioresorcinol, b₁₈ $150-1^\circ$; diAc., m. 49° .⁴⁸⁴

2,4-Dimethyldithioresorcinol, m. 121° .⁴⁸³

4-Ethyldithioresorcinol, b₂₀ $150-2^\circ$.⁴⁸³

- 2,5-Dichlorodithioresorcinol, m. 85° .²³⁵
1,4-Naphthalenedithiol, m. 181° ; b_{15} 210° .²⁵⁶
1,5-Naphthalenedithiol, m. 119° ,¹³⁹ $118-21^{\circ}$.^{411b}
2,6-Naphthalenedithiol, 196.5° ,^{411b} 178° .⁹⁷
2,7-Naphthalenedithiol, m. 187° ,^{411b} 181° ,²⁵⁶ 174° .¹⁷⁴
2,2'-Dimercaptobiphenyl, m. 79° .³⁵
4,4'-Dimercaptobiphenyl, m. $179-81^{\circ}$,^{411b} 176° .²³¹
9,10-Anthracenedimethanethiol, m. 145° .⁶⁰⁷

BIBLIOGRAPHY

1. Roger Adams, H. B. Bramlet and F. H. Tendick, J. Am. Chem. Soc., *42*, 2369-74 (1920)—C.A. *15*, 672.
2. Alexander and Posnansky, Fr. pat. 787,810 (1935); Ger. pat. 658,128 (1939)—C.A. *30*, 1068; *33*, 6653.
3. C. C. Allen to Shell Dev. Co., U.S. pat. 2,051,806 (1936)—C.A. *30*, 6760.
4. A. M. Alvarado to DuPont Co., U.S. pat. 2,402,586 (1946)—C.A. *40*, 5769.
5. Anon, Chem. Eng., *58*, 176-9 (1951)—C.A. *45*, 4914.
6. R. Anschütz and H. Reitter, Die Distillation, 2nd Edition, Bonn, Friedrich Cohen, 1895.
7. Antweiler, Dissertation Univ. Bonn, 1935.
8. A. E. Arbuzov and V. M. Zorastrova, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk, *1952*, 453-8—C.A. *47*, 4833.
9. F. Arndt with E. Milde and G. Eckert, Ber., *54*, 2236-42 (1921)—C.A. *16*, 1.
10. R. C. Arnold, P. J. Launer, and A. P. Lien, Anal. Chem., *24*, 1741-4 (1952)—C.A. *47*, 5673.
11. R. C. Arnold, A. P. Lieu, and R. M. Alm, J. Am. Chem. Soc., *72*, 731-3 (1950).
12. A. H. W. Aten, Jr., J. Chem. Phys., *5*, 260-3 (1937)—C.A. *31*, 3755.
13. V. Auger and M. Billy, Compt. rend., *136*, 555-6 (1901).
14. W. Autenrieth and Fritz Beuttel, Ber., *42*, 4346-57 (1909)—C.A. *4*, 457.
15. W. Autenrieth and Alfred Geyer, Ber., *41*, 4249-56 (1908)—C.A. *3*, 646.
16. W. Autenrieth and R. Hennings, Ber., *34*, 1772-8 (1901).
17. W. Autenrieth and K. Wolff, Ber., *32*, 1368-75 (1899).
18. K. Auwers and M. Dohrn, Z. physik. Chem., *30*, 529-44 (1899).

19. G. W. Ayers, Jr., *Oil & Gas J.*, 28, No. 20, 201, 204, 374 (1929)—C.A. 24, 1732.
20. H. J. Backer, *Rec. trav. chim.*, 54, 215–8 (1935)—C.A. 29, 2914.
21. H. J. Backer and N. D. Dijkstra, *Rec. trav. chim.*, 51, 289–93 (1932)—C.A. 26, 2432.
22. H. J. Backer and J. Kramer, *Rec. trav. chim.*, 53, 1101–12 (1934)—C.A. 29, 1061.
23. H. J. Backer and P. L. Stedehouder, *Rec. trav. chim.*, 52, 437–53 (1933)—C.A. 27, 5055.
24. H. J. Backer and A. F. Tamsma, *Rec. trav. chim.*, 57, 1183–1210 (1938)—C.A. 33, 1679.
25. H. J. Backer, P. Terpstra, and N. D. Dykstra, *Rec. trav. chim.*, 51, 1166–72 (1932)—C.A. 27, 491.
26. H. Bader, L. C. Cross, Ian Heilbron, and E. R. H. Jones, *J. Chem. Soc.*, 1949, 619–23—C.A. 43, 7417.
27. D. E. Badertscher, H. L. Coonradt, and D. J. Crowley to Socony-Vac. Oil Co., U.S. pat. 2,386,769, 2,386,771, 2,386,772, 2,386,774, 2,387,224 (1945)—C.A. 40, 584.
28. D. E. Badertscher, D. J. Crowley, and C. F. Feasley, to Socony-Vac. Oil Co., U.S. pat. 2,386,773 (1945)—C.A. 40, 584–5.
29. Badische Anilin- & Soda-Fabrik, *Ger. pat.* 871,447 (1953)—C.A. 48, 1411.
30. Hans Bähr and Hubert Corr to I. G. Farben., *Ger. pat.* 708,261 (1941)—C.A. 37, 2744.
31. J. E. Baer and Marvin Carmack, *J. Am. Chem. Soc.*, 71, 1215–1218 (1949)—C.A. 43, 6511.
32. Balard, *Ann. chim. phys.*, (3) 12, 294–330 (1844)—*Ann.*, 52, 312–3 (1844).
33. M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 1950, 309–12—C.A. 45, 6174.
34. S. A. Ballard and D. E. Winkler to Shell Dev. Co., U.S. pat. 2,438,838 (1948)—C.A. 42, 4609.
35. H. J. Barber and Samuel Smiles, *J. Chem. Soc.*, 1928, 1141–9—C.A. 22, 3153.
36. Charles Barkenbus, E. B. Friedman, and R. K. Flege, *J. Am. Chem. Soc.*, 49, 2549–53 (1927)—C.A. 21, 3899.
37. A. Baroni, *Atti accad. Lincei*, 12, 234–7 (1930); 27, 238–42 (1938)—C.A. 25, 2687; 33, 163.
38. F. T. Barr and D. B. Keyes, *Ind. Eng. Chem.*, 26, 1111–4 (1934)—C.A. 28, 7124.

39. J. M. Barron, A. R. Vanderploeg, and Hubert McReynolds, *Ind. Eng. Chem.*, **41**, 2687-90 (1949)—C.A. **44**, 2214.
40. G. M. Barrow and K. S. Pitzer, *Ind. Eng. Chem.*, **41**, 2737-40 (1949)—C.A. **44**, 2361.
41. Karl Bauer to I. G. Farben., U.S. pat. 2,116,182 (1938)—C.A. **32**, 5002.
42. Richard Bauer, *Z. physiol. Chem.*, **35**, 343-57 (1902).
43. E. Baumann, *Ber.*, **23**, 1869-76 (1890).
44. E. Baumann and Emil Fromm, *Ber.*, **28**, 910 (1895).
45. E. Baumann and Preusse, *Z. physiol. Chem.*, **5**, 319 (1881).
46. E. Baumann and Schmitz, *Z. physiol. Chem.*, **20**, 591, 593 (1895).
47. J. J. Beanblossom and R. H. Kimball to Hooker Electro-Chem. Co., U.S. pat. 2,404,425 (1946)—C.A. **40**, 6496.
48. Ernst Beckmann, *Pharm. Central H.*, **37**, 557 (1896)—C. **1896**, II 673.
49. E. O. Beckmann, *J. prakt. Chem.*, (2) **17**, 439-76 (1878).
50. Friedrich Beilstein and A. Kurbatow, *Ann.*, **197**, 75-85 (1897).
51. F. K. Bell, *Ber.*, **60**, 1749-56 (1927); **61**, 1918-23 (1928)—C.A. **21**, 3828; **23**, 36.
52. R. T. Bell to Pure Oil Co., U.S. pat. 2,441,385 (1948); 2,531,602 (1950); 2,565,195 (1951); 2,647,151 (1953)—C.A. **42**, 6375; **45**, 3407; **46**, 3555; **48**, 7623.
53. R. T. Bell and C. M. Thacker to Pure Oil Co., U.S. pat. 2,479,996 (1949); 2,498,872, 2,531,601 (1950)—C.A. **44**, 5377; **45**, 638, 3407.
54. Rezső Benkö, *Hung. pat.* 124,337 (1940)—C.A. **34**, 7298.
55. G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, **1927**, 1666-76—C.A. **21**, 3191.
56. Hilding Bergström and K. G. Trobeck, *Svensk Papperstidn*, **42**, 554-7 (1939)—C.A. **34**, 1171.
57. Seymour Bernstein and K. J. Sax to Am. Cyanamid Co., U.S. pat. 2,582,918 (1952)—C.A. **46**, 8154.
58. A. Bernthsen and H. Klinger, *Ber.*, **11**, 492-5 (1878); **12**, 574-6 (1879).
59. M. P. E. Berthelot, *Compt. rend.*, **132**, 55 (1901).
60. A. Berthoud and R. Brum, *J. chim. phys.*, **21**, 143-60 (1924)—C.A. **19**, 35.
61. Silvio Bezzi, (a) *Gaz. chim. ital.*, **65**, 693-703 (1935); (b) *ibid.*, 704-23 (1935)—C.A. **30**, 2171, 2172.

62. Silvio Bezzi and Pietro Lanza, *Gaz. chim. ital.*, **80**, 180-8 (1950)—C.A. **45**, 3798.
63. C. T. Bhatt, K. S. Nargund, D. D. Kanga, and M. S. Shah, *J. Univ. Bombay*, **3**, 159-60 (1934)—C.A. **29**, 4762.
64. Alfred Biedermann, *Ber.*, **19**, 1615 (1886).
65. Einar Biilmann, *Ann.*, **339**, 351-72 (1905); **348**, 120-43 (1906).
66. J. L. Binder, *J. Chem. Phys.*, **17**, 499-500 (1949)—C.A. **43**, 7804.
67. E. C. Bingham and H. J. Fornwalt, (a) *Science*, **71**, 564-5 (1930); (b) *Rheol.*, **1**, 372-417 (1930)—C.A. **24**, 3935, 5191.
68. S. F. Birch, *J. Inst. Petroleum*, **39**, 185-205 (1953)—C.A. **47**, 10211.
69. S. F. Birch and W. S. G. P. Norris, *J. Chem. Soc.*, **127**, 898-907 (1925)—C.A. **19**, 2407.
70. J. H. Birkinshaw, W. P. K. Findlay, and R. A. Webb, *Biochem. J.*, **36**, 526-9 (1942)—C.A. **37**, 409.
71. A. P. Bjerregaard, *Ind. Eng. Chem.*, **17**, 142-4 (1925)—C.A. **19**, 889.
72. Stanley Blackburn and Frederick Challenger, *J. Chem. Soc.*, **1938**, 1872-8—C.A. **33**, 1265.
73. O. C. Blade, U.S. Bureau of Mines Inf. Circular, *No. 7042* (1938)—C.A. **33**, 1876.
74. J. J. Blanksma, *Rec. trav. chim.*, **20**, 400 (1901).
75. J. Böescken and N. v. d. Linde, *Rec. trav. chim.*, **54**, 739-44 (1935)—C.A. **30**, 2912.
76. Horst Böhme and Joachim Wagner, *Ber.*, **75B**, 606-14 (1942)—C.A. **37**, 3342.
77. J. W. Boenigk, J. E. Christian and G. L. Jenkins, *J. Am. Pharm. Assoc.*, **38**, 357-60 (1949)—C.A. **44**, 1443.
78. M. T. Bogert and M. R. Mandelbaum, *J. Am. Chem. Soc.*, **45**, 3045-55 (1923)—C.A. **18**, 1822.
79. F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75**, 6019-22 (1953).
80. F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082-5 (1954).
81. R. W. Borgeson and J. A. Wilkinson, *J. Am. Chem. Soc.*, **51**, 1453-6 (1929)—C.A. **23**, 3148.
82. J. N. Borglin and Emil Ott to Hercules Powder Co., (a) U.S. pat. 2,052,210 (1936); (b) 2,076,875 (1937)—C.A. **30**, 7089; **31**, 4017.
83. Walther Borsche and W. Lange, (a) *Ber.*, **39**, 392-7 (1906); (b) *ibid.*, **40**, 2220-5 (1907)—C.A. **1**, 2555.

84. R. Boudet and R. Rambaud, *Bull. soc. chim. France*, 1948, 793, 804—C.A. 43, 13.
85. Edward Bourgeois, *Rec. trav. chim.*, 18, 426–50 (1899).
86. Edward Bourgeois and A. Abraham, *Rec. trav. chim.*, 30, 407–425 (1911)—C.A. 6, 623.
87. K. Brand and K. W. Kranz, *J. prakt. Chem.*, (2) 115, 143–62 (1927)—C.A. 21, 1105.
88. K. Brand and H. W. Leyerzapf, *Ber.*, 70, 284–96 (1937)—C.A. 31, 3461.
89. K. Brand, O. Stallmann, W. Groebe, and H. Stein, *J. prakt. Chem.*, (2) 109, 1–40 (1925)—C.A. 19, 1257.
90. R. R. Brattain, *Petroleum World*, 50, No. 2, 46–56 (1943); *Pet. Refiner*, 22, 104–10 (1943)—C.A. 37, 3700.
91. Julius von Braun, (a) *Ber.*, 42, 4568–74 (1909); (b) *ibid.*, 45, 1563–7 (1912)—C.A. 4, 592; 6, 2616.
92. Julius von Braun and Gottfried Manz, *Ann.*, 468, 258–77 (1929)—C.A. 23, 2709.
93. Julius von Braun, Wilhelm May and Robert Michaelis, *Ann.*, 490, 189–200 (1931)—C.A. 26, 703.
94. Julius von Braun and Robert Murjahn with E. Hahn, *Ber.*, 59, 1202–9 (1926)—C.A. 20, 2991.
95. Julius von Braun and Theodor Plate, *Ber.*, 67, 281–5 (1934)—C.A. 28, 2323.
96. Julius von Braun, Wilhelm Teuffert, and Karl Weissbach, *Ann.*, 472, 121–42 (1929)—C.A. 23, 4669.
97. L. Braun and R. Ebert, *Ber.*, 25, 2735 (1892).
98. A. Brjuchonenko, *J. prakt. Chem.*, (2) 59, 45–52, 596 (1899).
99. F. R. Brooks and A. C. Nixon, *J. Am. Chem. Soc.*, 75, 480 (1953)—C.A. 47, 5102.
100. J. W. Brooks, E. G. Howard, and J. J. Wehrle, *J. Am. Chem. Soc.*, 72, 1289–91 (1950)—C.A. 44, 6410.
101. A. S. Broun, M. G. Voronkov, and K. P. Katkova, *J. Gen. Chem. (USSR)*, 20, 726–37, 765–76 (Engl. translation) (1950)—C.A. 44, 7755; 45, 7948.
102. F. E. Brown and J. E. Snyder, *J. Am. Chem. Soc.*, 48, 1926–8 (1926)—C.A. 20, 2481.
103. R. Brown, W. E. Jones and A. R. Pinder, *J. Chem. Soc.*, 1951, 2123–5—C.A. 46, 2486.
104. Horst Brückner, *Chem. Fabrik*, 1939, 480–93—C.A. 34, 872.
105. Hans Bunte, *Ber.*, 7, 646–8 (1874).
106. W. J. Burke to DuPont Co., U.S. pat. 2,212,150 (1940)—C.A. 35, 464.

107. P. D. Caesar and P. D. Branton, *Ind. Eng. Chem.*, **44**, 122-5 (1952)—C.A. **46**, 7089.
108. Paul Cagniant, *Compt. rend.*, **229**, 1342-3 (1949)—C.A. **44**, 4459.
109. August Cahours and A. W. Hofmann, *Ann.*, **102**, 291-292 (1857).
110. T. L. Cairns, G. L. Jones, A. W. Larchar, and B. C. McKusick, *J. Am. Chem. Soc.*, **74**, 3982-9 (1952)—C.A. **47**, 4283.
111. L. Carius, *Ann.*, **122**, 71-7 (1862).
112. W. H. Carothers and G. J. Berchet to DuPont, U.S. pat. 2,136,178 (1938)—C.A. **33**, 1345.
113. G. Carrara and A. Coppadoro, *Gaz. chim. ital.*, **33**, I, 329-53 (1903).
114. Frederick Challenger, *Chemistry and Industry*, **48**, 622-6 (1929); *Brennstoff Chem.*, **10**, 277-9 (1929)—C.A. **23**, 4332; **24**, 493.
115. Frederick Challenger and D. Greenwood, *Biochem. J.*, **44**, 87-91 (1949)—C.A. **43**, 6286.
116. Frederick Challenger and J. B. Harrison, *J. Inst. Petroleum Tech.*, **21**, 135-54, 169-71 (1935)—C.A. **29**, 4006.
117. Frederick Challenger, J. A. R. Jinks, and John Haslam, *J. Chem. Soc.*, **127**, 162-6 (1925)—C.A. **19**, 1139.
118. Frederick Challenger and A. A. Rawlings, *J. Chem. Soc.*, **1937**, 868-75—C.A. **31**, 5321.
119. Georges Champetier, Yves Étienne, and Robert Kullmann, *Compt. rend.*, **234**, 1985-6 (1952)—C.A. **46**, 8559.
120. J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, **1950**, 579-85—C.A. **44**, 6810.
121. K. Charitschkov, *J. Russ. Phys. Chem. Soc.*, **31**, 655-8 (1899)—C. **1899**, II, 920.
122. Chem. Fabr. von Heyden, A.-G., Ger. pat. 497,570 (1928)—C.A. **24**, 4054.
123. T. Chruszcz and J. Reszetniak, *Przemysl Chem.*, **18**, 360-3 (1934)—C.A. **29**, 5982.
124. L. Chugaev, *Ber.*, **42**, 49-54 (1909)—C.A. **3**, 902.
125. M. R. Cines, U.S. pat. 2,602,093 (1952)—C.A. **46**, 10604.
126. M. Claasz, *Ber.*, **45**, 2424-8 (1912).
127. L. H. Clark and C. W. Deibel to Sharples Solvents Corp., U.S. pat. 2,147,400 (1939)—C.A. **33**, 3809.
128. A. Claus, (a) *Ber.*, **5**, 659-61 (1872); **8**, 532 (1875); (b) *Ann.*, **179**, 145-8 (1875).
129. L. W. Clemence and M. T. Leffler, *J. Am. Chem. Soc.*, **70**, 2439-40 (1948)—C.A. **42**, 8154.

130. F. F. Cleveland, M. J. Murray, and R. H. Saunders, *Phys. Rev.* **61**, 386 (1941)—C.A. **37**, 2990.
131. Archibald Clow and J. M. C. Thompson, *Trans. Faraday Soc.*, **33**, 894–904 (1937)—C.A. **31**, 6941.
132. J. B. Cohen and F. W. Skirrow, *J. Chem. Soc.*, **75**, 887–93 (1899).
133. J. E. Cole to DuPont Co., U.S. pat. 2,148,106 (1939)—C.A. **33**, 3813.
134. R. M. Cole and D. D. Davidson, *Ind. Eng. Chem.*, **41**, 2711–5 (1949)—C.A. **44**, 2216.
135. G. Collin, T. P. Hilditch, P. Marsh, and A. F. McLeod, *J. Soc. Chem. Ind.*, **52**, 272–5T (1933)—C.A. **28**, 1984.
136. Henry Cooney, Refiner, Natural Gasoline Mfr., **7**, No. 9, 92, 96 (1928)—C.A. **23**, 965.
137. A. C. Cope and Eugene Farkas, *J. Org. Chem.*, **19**, 385–90 (1954)—C.A. **49**, 4541.
138. M. J. Copley, C. S. Marvel, and Emanuel Ginsberg, *J. Am. Chem. Soc.*, **61**, 3161–2 (1939)—C.A. **34**, 396.
139. A. Corbellini and L. Albenga, *Gaz. chim. ital.*, **61**, 111–30 (1931)—C.A. **25**, 3340.
140. J. M. Crafts, *Ber.*, **19**, 3130 (1886).
141. Blick Crawley and R. H. Griffith, *J. Chem. Soc.*, **1938**, 720–3—C.A. **32**, 6138.
142. Elizabeth A. Crigler, *J. Am. Chem. Soc.*, **54**, 4199–206 (1932)—C.A. **26**, 377.
143. Ugo Croatto, Antonio Fava, and Vladimiro Scatturin, *Ricerca sci.*, **19**, 875–6 (1949)—C.A. **45**, 4107.
144. D. J. Crowley and A. I. Kosak to Socony-Vac. Oil Co., U.S. pat. 2,490,257 (1949)—C.A. **44**, 4502.
145. C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, **1949**, 282–7 (1949)—C.A. **43**, 7419.
146. J. I. Cunneen, *J. Chem. Soc.*, **1947**, 134–41; *J. Appl. Chem.*, **2**, 353–7 (1952)—C.A. **41**, 5093; **48**, 3275.
147. G. O. Curme, Jr., and H. R. Curme, *Chem. Met. Eng.*, **25**, 957–9 (1921)—C.A. **16**, 553.
148. Daccomo, *Jahrb.*, **1891**, 1377.
149. N. C. Dacu, *Mon. petrole roumain*, **40**, 151–3 (1939)—C.A. **33**, 9604.
150. A. Dadieu, A. Pongratz, and K. W. F. Kohlrausch, (a) *Sitzber. Akad. Wiss. Wien, Math-naturw. Klasse*, **141**, 267–81 (1932); (b) *ibid.*, 477–92; *Monatsh.*, **61**, 409–25 (1932)—C.A. **27**, 902, 4172.
151. J. B. Davidson and J. P. Olin to Sharples Chemicals Inc., U.S. pat. 2,494,610 (1950)—C.A. **44**, 3726.

152. Norman Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316-24 (1942)—C.A. **36**, 1836.
153. H. W. Davis, Private communication.
154. L. L. Davis, B. H. Lincoln, and G. D. Byrket to Continental Oil Co., U.S. pat. 2,238,790 (1941)—C.A. **35**, 4778.
155. Marcel Delepine, *Compt. rend.*, **153**, 725-7 (1911); *Ann. chim. phys.*, (8) **25**, 529-74 (1912)—C.A. **6**, 351, 1608.
156. R. L. Denyer, F. A. Fidler, and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2727-37 (1949)—C.A. **44**, 2735.
157. Martin De Simo and J. J. O'Connor to Shell Dev. Co., U.S. pat. 2,346,102 (1944)—C.A. **38**, 4958.
158. Alice M. Dessert to Am. Cyanamid Co., U.S. pat. 2,519,310 (1950)—C.A. **45**, 668.
159. D. H. Desty and F. A. Fidler, *Ind. Eng. Chem.*, **43**, 905-10 (1951)—C.A. **45**, 5916.
160. Deut. Gold- und Silber-Scheideanstalt, (a) *Brit. pat.* 453,859 (1936); (b) *Fr. pat.* 804,112 (1936); *Ger. pat.* 665,370 (1938)—C.A. **31**, 1042, 2617; **33**, 1760.
161. Paul Diergart, *J. prakt. Chem.*, [2] **99**, 281-92 (1919)—C.A. **14**, 935.
162. Leonard Dobbin, *J. Chem. Soc.*, **57**, 641 (1890); *Chem. News*, **61**, 312 (1890).
163. J. J. Donleavy and James English, Jr., *J. Am. Chem. Soc.*, **62**, 2965-6 (1940)—C.A. **35**, 85.
164. F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 970-7 (1951)—C.A. **46**, 8037.
165. Jules Duchesne, (a) *Bull. soc. roy. sci. Liege*, **10**, 480-96, 506-19 (1941); (b) *Nature*, **159**, 62-3 (1947)—C.A. **37**, 2233; **41**, 2289.
166. A. Dudenko, *Azerbaidzhanskoe Neftyanoe Khozyaistvo*, **1931**, No. 6, 42-4—C.A. **26**, 289.
167. H. R. Duffey, R. D. Snow, and D. B. Keyes, *Ind. Eng. Chem.*, **26**, 91-3 (1934)—C.A. **28**, 1255.
168. J. Dumas, *Ann.*, **16**, 171 (1835).
169. A. E. Dunstan, *Z. physik. Chem.*, **49**, 590-6 (1904); *J. Chem. Soc.*, **85**, 817-27 (1904).
170. E. I. duPont de Nemours & Co., (a) *Brit. pat.* 442,730 (1936); (b) 577,279 (1946); (c) 574,936 (1946)—C.A. **30**, 5052; **42**, 6374; **43**, 2629.
171. E. I. duPont de Nemours & Co. and F. K. Signaigo, *Brit. pat.* 577,013 (1946)—C.A. **42**, 6380.
172. J. L. Eaton and J. B. Fenn to Sharples Chemicals, Inc., U.S. pat. 2,468,739 (1949)—C.A. **43**, 5790.

173. J. L. Eaton and J. F. Olin to Sharples Chemicals, Inc., U.S. pat. 2,443,852 (1948)—C.A. 42, 7313.
174. R. Ebert and E. Kleiner, Ber., 24, 144 (1891).
175. L. T. Eby to S. O. Dev. Co., (a) U.S. pat. 2,382,700 (1945); (b) 2,472,470 (1949)—C.A. 40, 723; 43, 6646.
176. A. Edinger, Ber., 41, 937-43 (1908)—C.A. 2, 1975.
177. W. F. Edwards, Am. Chem. J., 17, 473-506 (1895).
178. H. E. Eggers, J. Phys. Chem., 8, 14-36 (1904)—C. 1904, I, 1390.
179. Gustav Egloff and J. C. Morrell, Chem. & Met. Eng., 28, 633-5 (1923)—C.A. 17, 2046.
180. Fritz Eisenlohr, Ber., 44, 3188-207 (1911)—C.A. 6, 485.
181. Eberhard Elbel and Alfred Kirstahler to Henkel & Cie., U.S. pat. 2,031,529 (1936)—C.A. 30, 2202.
182. Eberhard Elbel and E. L. Müller to Henkel & Cie., U.S. pat. 2,050,169 (1936)—C.A. 30, 6854.
183. J. W. Ellis, J. Am. Chem. Soc., 50, 2113-8 (1928)—C.A. 22, 3355.
184. L. M. Ellis, Jr., and E. E. Reid, J. Am. Chem. Soc., 54, 1674-87 (1932)—C.A. 26, 2697.
185. M. A. El'yashevich and M. V. Vol'kenshtein, Compt. rend. acad. sci. URSS., 41, 366-8 (1943)—C.A. 38, 6197.
186. H. Endemann, Ann., 140, 336 (1866).
187. E. Erlenmeyer and J. A. Wanklyn, Ann., 135, 129-5 (1865).
188. T. W. Evans, W. E. Vaughn, and F. F. Rust, U.S. pat. 2,376,675 (1945)—C.A. 39, 3533.
189. W. F. Faragher, J. C. Morrell, and S. Comay, Ind. Eng. Chem., 20, 527-32 (1928)—C.A. 22, 2459.
190. M. W. Farlow and F. K. Signaigo to DuPont Co., (a) U.S. pat. 2,402,613, 2,402,615 (1946); (b) 2,402,614 (1946)—C.A. 40, 5758, 5760, 5763.
191. Heinrich Fasbender, (a) Ber., 20, 460-5 (1887); (b) *ibid.*, 21, 1473-7 (1888).
192. A. Favorskii, Bull. soc. chim., (4) 43, 551-63 (1928)—C.A. 22, 4199.
193. V. F. Felicetta, Q. P. Peniston, and J. L. McCarthy, Can. Pulp Paper Ind., 5, No. 12, 16, 18, 20, 22, 24, 26-7, 30, 41 (1952); Tappi, 36, 425-32 (1953)—C.A. 47, 5115, 12810.
194. J. B. Fenn and J. L. Eaton to Sharples Chemicals, Inc., U.S. pat. 2,481,583 (1949)—C.A. 44, 5376.
195. J. U. Ferran, Quim. e Industria, 2, 169-170 (1925)—C.A. 19, 3477.
196. D. L. Ferretto, Gaz. chim. ital., 30, I, 296-302 (1900).

197. G. A. Fester and F. A. Bertuzzi, *Rev. facultad quim. ind. agr. (Univ. nac. litoral, Santa Fe, Argentina)*, **5**, 85-7 (1937)—C.A. **31**, 7966.
198. Lamar Field and F. A. Grunwald, *J. Org. Chem.*, **16**, 946-53 (1951)—C.A. **46**, 1483.
199. L. F. Fieser, *J. Am. Chem. Soc.*, **52**, 5204-41 (1931)—C.A. **25**, 503.
200. L. F. Fieser and R. B. Turner, *J. Am. Chem. Soc.*, **69**, 2336 (1947)—C.A. **42**, 1250.
201. H. L. Finke, D. W. Scott, M. E. Gross, Guy Waddington, and H. M. Huffman, *J. Am. Chem. Soc.*, **74**, 2804-6 (1952)—C.A. **46**, 9364.
202. Cesare Finzi, *Gaz. chim. ital.*, **43**, II, 643-54 (1913)—C.A. **8**, 1757.
203. Emil Fischer, *Ber.*, **48**, 93-102 (1915)—C.A. **9**, 1057.
204. Emil Fischer and Werner Lipschitz, *Ber.*, **48**, 360 (1915)—C.A. **9**, 1483.
205. Emil Fischer and Franz Penzoldt, *Z. Naturw.*, (4) **5**, 263-C. 1886, 947; *Ann.*, **239**, 131-6 (1887).
206. B. Flaschenträger and G. Wannschaff, *Ber.*, **67**, 1121-4 (1934)—C.A. **28**, 5401.
207. W. H. Fletcher, *J. Am. Chem. Soc.*, **68**, 2726-8 (1946)—C.A. **41**, 1144.
208. F. A. Fluckiger, *Ber.*, **9**, 468-74 (1876).
209. D. G. Foster, *J. Am. Chem. Soc.*, **61**, 2972-3 (1939); *Org. Syntheses*, **24**, 89-92 (1944)—C.A. **34**, 396; **38**, 5808.
210. M. J. Fowle and R. D. Bent, *Oil & Gas J.*, **46**, No. 28, 209-15—C.A. **42**, 1725.
211. A. L. Fox to DuPont Co., (a) U.S. pat. 2,351,196 (1944); (b) 2,407,265, 2,407,266 (1946); *Brit. pat.* 580,366 (1946)—C.A. **38**, 5226; **41**, 1710, 3128.
212. J. J. Fox and F. G. Pope, *J. Chem. Soc.*, **103**, 1263-6 (1913)—C.A. **7**, 3317.
213. R. L. Frank and P. V. Smith, *J. Am. Chem. Soc.*, **68**, 2103-4 (1946)—C.A. **41**, 87.
214. R. L. Frank, P. V. Smith, F. W. Woodward, W. B. Reynolds, and P. J. Canterino, *J. Polymer Sci.*, **3**, 39-49 (1948)—C.A. **42**, 3986.
215. Adolf Franke and Rudolf Dworzak, *Monatsh.*, **43**, 661-71 (1923)—C.A. **17**, 2103.
216. J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023-6 (1952)—C.A. **46**, 5379.

217. P. Frasseti, *Ber.*, 38, 488-92 (1905).
218. Gerhard Free, Oel, Kohle, Erdoel, Teer, 12, 311-8 (1936)—*C.A.* 30, 6173.
219. F. A. French and R. S. Rasmussen, *J. Chem. Phys.*, 14, 389-94 (1946)—*C.A.* 40, 4603.
220. R. Fricke and G. Spilker, *Ber.*, 58, 24-6, 1589-601 (1925), 59, 349 (1926)—*C.A.* 19, 1412; 20, 193, 1804.
221. F. Fridau, *Ann.*, 83, 1-39 (1852).
222. P. Friedländer, *Ber.*, 39, 1065 (1906).
223. P. Friedländer and F. Mauthner, *Z. f. Farben- u. Textilchemie*, 3, 333-37—*C.* 1904, II, 1176.
224. P. Friedländer and A. Simon, *Ber.*, 55, 3969-80 (1922)—*C.A.* 17, 2880.
225. Walter Friedmann, *Ger. pat.* 296,986 (1917)—*C.* 1917, I, 717.
226. Emil Fromm and Oscar Achert, *Ber.*, 36, 545 (1903).
227. Emil Fromm and Heinrich Jörg, *Ber.*, 58, 304-9 (1925)—*C.A.* 19, 1557.
228. Emil Fromm and J. Wittmann, *Ber.*, 41, 2264-73 (1908)—*C.A.* 2, 2932.
229. Hiroichi Fukada, *J. Pharm. Soc. Japan*, 72, 1472-3 (1952)—*C.A.* 47, 8706.
230. Yoshishige Fukumoto, (a) *Sci. Repts. Tohoku Imp. Univ.*, (1) 23, 62-75 (1934); 25, 1162-9 (1937); (b) *J. Chem., Phys.*, 3, 164-8 (1935)—*C.A.* 28, 4312; 31, 5273; 29, 2848.
231. S. Gabriel and A. Deutsch, *Ber.*, 13, 386-91 (1880).
232. S. M. Gabriel'yantz and O. A. Artem'eva, *Groznenskii Neftyanik*, 4, No. 8, 41-5 (1934)—*C.A.* 29, 2725.
233. Ludwig Gattermann, *Ber.*, 32, 1136-46, 1147 (1899).
234. C. Gautier, *Compt. rend. soc. biol.*, 89, 239 (1923)—*C.A.* 18, 109.
235. Erich Gebauer-Fülneegg and Hans Figdor, *Monatsh.*, 48, 645-58 (1927)—*C.A.* 22, 1148.
236. Sigbert Genelin, *Z. phys. chem. Unterricht*, 43, 80-1 (1930)—*C.A.* 25, 445.
237. Gustav Gerlich, *Ann.*, 178, 80-91 (1875).
238. P. N. Ghosh and B. D. Chatterjee, *Z. Physik*, 72, 542-52 (1931)—*C.A.* 26, 2117.
239. D. T. Gibson, *J. Chem. Soc.*, 1930, 12-4—*C.A.* 24, 1843.
240. F. A. Gilfillan, *J. Am. Chem. Soc.*, 44, 1323-33 (1922)—*C.A.* 16, 2304.

241. Henry Gilman and H. S. Broadbent, *J. Am. Chem. Soc.*, **69**, 2053-7 (1947)—C.A. **42**, 145.
242. Henry Gilman and Lawrence Fullhart, *J. Am. Chem. Soc.*, **71**, 1478-81 (1949)—C.A. **43**, 6574.
243. Henry Gilman and A. P. Hewlet, *J. Am. Chem. Soc.*, **52**, 2141-4 (1930)—C.A. **24**, 3011.
244. Henry Gilman and K. E. Lentz, *J. Am. Chem. Soc.*, **74**, 1107 (1952)—C.A. **47**, 11215.
245. G. M. Ginodman, *Bumazh. Prom.*, **22**, No. 7, 16-22 (1947); *Gigiena i Sanit.*, **13**, No. 7, 11-14 (1948)—C.A. **42**, 6111; **43**, 8135.
246. Michele Giua and Antonio Ruggeri, *Gaz. chim. ital.*, **53**, 344 (1923).
247. J. H. Gladstone, *Chem. News*, **55**, 302 (1887).
248. Walter Gordy and S. C. Stanford, *J. Am. Chem. Soc.*, **62**, 497-505 (1940)—C.A. **34**, 2705.
249. N. Grabousky and A. Saytzeff, *Ann.*, **171**, 251-8 (1874).
250. E. Grandjean-Hirter, *Deut. med. Wochenschr.*, **42**, 1316-8—C. **1916**, II, 1181.
251. H. LeB. Gray and G. O. Gutekunst, *J. Am. Chem. Soc.*, **42**, 856-60 (1920)—C.A. **14**, 1829.
252. B. S. Greensfelder and R. J. Moore to Shell Dev. Co., *Brit. pat.* 603,103 (1948)—C.A. **43**, 691.
253. Gregory, *Ann.*, **15**, 239-40 (1835).
254. C. H. Grogan, L. M. Rice, and M. X. Sullivan, *J. Org. Chem.*, **18**, 728-35 (1953)—C.A. **48**, 6967.
255. H. P. A. Groll and J. C. Ott to Shell Oil Co., *U.S. pat.* 2,097,155 (1937)—C.A. **32**, 194.
256. L. Grosjean, *Ber.*, **23**, 2370-1 (1890).
257. P. C. Guha and M. N. Chakladar, *Q. J. Indian Chem. Soc.*, **2**, 318-35 (1925)—C.A. **20**, 1797.
258. S. L. Gusinskaya, *Acta Univ. Asiae Mediae, Serv. VI, Chemia, No. 42*, 6 p. (1938) (English summary)—C.A. **34**, 3482.
259. J. E. Hackford, *J. Inst. Pet. Techn.*, **12**, 135-6 (1926).
260. L. Hagelberg, *Ber.*, **23**, 1083-92 (1890).
261. J. E. Haggmacher, *J. Am. Chem. Soc.*, **68**, 1633-4 (1946)—C.A. **40**, 5987.
262. W. E. Haines, R. V. Helm, C. W. Bailey, and J. S. Ball, *J. Phys. Chem.*, **58**, 270-78 (1954).
263. J. H. Hale, M. C. Simmons, and F. P. Whisenhunt, *Ind. Eng. Chem.*, **41**, 2702-8 (1949)—C.A. **44**, 2212.
264. J. H. Hale, C. J. Thompson, M. G. Barker, H. M. Smith,

- and J. S. Ball, *Anal. Chem.*, **23**, 287-93 (1951)—C.A. **45**, 5395.
265. W. J. Hale to Dow Chem. Co., U.S. pat. 1,825,662 (1931)—C.A. **26**, 480.
266. W. P. Hall and E. E. Reid, *J. Am. Chem. Soc.*, **65**, 1466-8 (1943)—C.A. **37**, 5698.
267. Corwin Hansch and W. A. Blondon, *J. Am. Chem. Soc.*, **70**, 1561-3 (1948).
268. A. Hantzsch and H. Freese, *Ber.*, **28**, 3237-51 (1895).
269. Josef Haraszti, *J. prakt. Chem.*, [2] **149**, 301-10 (1937)—C.A. **32**, 528.
270. D. Hardin and S. Sikorsky, *J. chim. phys.*, **6**, 179-211 (1908)—C.A. **2**, 2073.
271. Dorothy Haresnape, F. A. Fidler, and R. A. Lowry, *Ind. Eng. Chem.*, **41**, 2691-7 (1949)—C.A. **44**, 2214.
272. W. D. Harkins, F. E. Brown, and E. C. H. Davies, *J. Am. Chem. Soc.*, **39**, 354-64 (1917)—C.A. **11**, 731.
273. W. D. Harkins, E. C. H. Davies, and G. L. Clark, *J. Am. Chem. Soc.*, **39**, 541-96 (1917)—C.A. **11**, 1588.
274. C. R. Hauser, S. W. Kantor, and W. R. Brasen, *J. Am. Chem. Soc.*, **75**, 2660-3 (1953).
275. Emeric Havas to Du Pont Co., U.S. pat. 1,993,663 (1935)—C.A. **29**, 2547.
276. Henkel & Cie., (a) *Fr. pat.* 746,609 (1933); *Brit. pat.* 401,118 (1933); (b) *Fr. pat.* 751,117 (1933); *Brit. pat.* 407,181 (1934)—C.A. **27**, 4717; **28**, 2571, 1049, 4745.
277. Louis Henry, *Ber.*, **2**, 495-7 (1869).
278. Louis Henry, (a) *Rec. trav. chim.*, **24**, 356 (1905); (b) *Bull. acad. roy. Belg.*, **1905**, 158-77; (c) *Bull. soc. chim. Belg.*, **1907**, 742-64; *Rec. trav. chim.*, **27**, 79-96 (1908); (d) *ibid.*, **28**, 444-8 (1909)—C. **1905**, II 214; C.A. **2**, 801, 2546; **4**, 766.
279. Louis Henry and A. Dewael, *Bull. acad. roy. Belg.*, **1908**, 957-63—C. **1909**, I, 1854.
280. A. H. Herz and D. S. Tarbell, *J. Am. Chem. Soc.*, **75**, 4657-60 (1953)—C.A. **48**, 12697.
281. R. W. Hess and J. M. F. Leaper to Barrett Co., U.S. pat. 1,729,615 (1929)—C.A. **23**, 5474.
282. Carl Hill and Joseph Sadomsky, *Ber.*, **24**, 2388 (1891).
283. J. M. Hirshon, D. M. Gardner, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).
284. F. W. Hobden, E. F. Johnston, L. H. P. Weldon, and C. L. Wilson, *J. Chem. Soc.*, **1939**, 61-7—C.A. **33**, 5730.

285. H. H. Hodgson and E. R. Ward, *J. Chem. Soc.*, 1949, 1187–90—C.A. 44, 3447.
286. H. H. Hodgson and J. H. Wilson, *J. Chem. Soc.*, 127, 440–4 (1925)—C.A. 19, 1412.
287. W. H. Hoffert and K. Wendtner, *J. Inst. Petroleum*, 35, 171–92 (1949)—C.A. 43, 5932.
288. A. W. Hofmann and Aug. Cahours, *J. Chem. Soc.*, 10, 320 (1858).
289. Bror Holmberg, (a) *J. prakt. Chem.*, [2] 71, 264–95 (1905); (b) *Archiv Kemi, Mineral. Geol.*, 12B, No. 47, 3 p. (1938); (c) *ibid.*, 13A, No. 8, 9 p. (1939)—C.A. 32, 4151; 33, 6278.
290. L. H. Horsley, *Anal. Chem.*, 19, 508–600 (1947)—C.A. 41, 6096.
291. A. Horstmann, *Ber.*, 20, 766–81 (1887).
292. Naotoshi Hoshi and Mitsuo Saito, *Japan pat.* 4717 ('52)—C.A. 48, 8260.
293. J. Houben and Hans Doescher, *Ber.*, 39, 3503–9 (1906).
294. T. van Hove, *Bull. acad. Belg.*, [5] 13, 206.
295. H. Hübner and Julius Alsberg, *Ann.*, 156, 325–31 (1870).
296. H. Hübner and J. Post, *Z. f. Chemie*, 6, 390 (1870); *Bull. soc. chim.*, [2] 6, 130–1 (1871).
297. W. J. Huff, *Proc. 2nd Intern. Conference Bituminous Coal*, 2, 814–5 (1928)—C.A. 23, 4047.
298. C.M. Hull to S. O. of Indiana, *U.S. pat.* 2,351,763 (1944)—C.A. 38, 5225.
299. E. Humann, *Ann.*, 95, 256 (1855); *Ann. chim. phys.*, [3] 44, 337 (1855).
300. E. C. E. Hunter and J. R. Partington, (a) *J. Chem. Soc.*, 1931, 2062–70; (b) *ibid.*, 1932, 2812–9—C.A. 25, 5674; 27, 1322.
301. J. H. Hunter to Upjohn Co., *U.S. pat.* 2,584,131 (1952)—C.A., 47, 7548.
302. C. D. Hurd and Harry Greengard, *J. Am. Chem. Soc.*, 52, 3356–8 (1930)—C.A. 24, 4771.
303. August Husemann, *Ann.*, 123, 83–90 (1862).
304. W. K. Hutchison, *Gas J.*, 220, 475–6, 479–85, 667—C.A. 32, 6437.
305. I. G. Farben., *Brit. pat.* 340,012 (1929); *Fr. pat.* 704,691 (1930)—C.A. 25, 2738, 4555.
306. I. G. Farben., *Brit. pat.* 444,262 (1936); *Fr. pat.* 797,606 (1936); *Brit. pat.* 450,760 (1936)—C.A. 30, 5590, 8244; 31, 114.

307. I. G. Farben., Brit. pat. 454,668 (1936); Fr. pat. 801,762 (1936)—C.A. 31, 1430.
308. I. G. Farben., Fr. pat. 793,151 (1936); Brit. pat. 444,689 (1936)—C.A. 30, 4240, 5594.
309. I. G. Farben., Ger. pat. 513,410 (1928); Fr. pat. 37,197 (1929); Brit. pat. 360,993 (1930)—C.A. 25, 1329, 2517; 27, 1890.
310. I. G. Farben. (Ernst Keyssner), Ger. pat. 669,961 (1939)—C.A. 33, 5415.
311. I. G. Farben. (Karl Keller), Ger. pat. 557,245 (1930); 559,739 (1930); 583,853 (1933)—C.A. 27, 310, 730; 28, 776.
312. Imperial Chemical Industries, Brit. pat. 580,514 (1946)—C.A. 41, 1881.
313. Internat. Nahrungs. Genussmittel, Ger. pat. 484,244 (1926); Swiss pat. 133,787 (1927)—C.A. 24, 865, 1652.
314. V. N. Ipatieff and B. S. Friedman, J. Am. Chem. Soc., 61, 71-4 (1939)—C.A. 33, 1659.
315. C. L. Jackson and G. T. Hartshorn, Am. Chem. J., 5, 264-91 (1884).
316. C. L. Jackson and J. F. White, Am. Chem. J., 2, 158-71 (1881).
317. Bernhard Jaeckel, Ber., 83, 578-82 (1950)—C.A. 45, 3340.
318. Jaworski, Z. Chemie, 1865, 222.
319. G. L. Jenkins and J. E. Christian, U.S. pat. 2,430,678, 2,430,679 (1947)—C.A. 42, 929.
320. E. M. Johansen to Gray Process Corp., (a) U.S. pat. 1,836,170; (b) 1,836,171 (1931)—C.A. 26, 995.
321. T. B. Johnson and J. M. Sprague, Science, 83, 528 (1936); J. Am. Chem. Soc., 58, 1348-51 (1936)—C.A. 30, 5186, 6703.
322. G. W. Jones, R. E. Kennedy, and W. E. Miller, U.S. Bur. of Mines, Report of Investigations, No. 3648, 6 p. (1942)—C.A. 36, 7319.
323. S. O. Jones and E. E. Reid, J. Am. Chem. Soc., 60, 2452-5 (1938)—C.A. 33, 126.
324. Herman Kahn, Bull. soc. chim. Roumania, 5, 70-2 (1923)—C.A. 18, 1467.
325. L. Kahovec and K. W. F. Kohlrausch, Z. physik. Chem., B 48, 7-11 (1940)—C.A. 35, 3172.
326. L. Kahovec and A. W. Reitz, Monatsh., 69, 363-76 (1936)—C.A. 31, 2515.
327. J. P. Karplus, Archiv path. Anat. u. Physiol., 131, 210-22 (1893).

328. M. A. Kazarnovskaya and A. S. Sosnina, O.N.T.I. Gorno-Geol.—Neftyanoe Izdat., 1934, 202–9—C.A. 29, 2707.
329. August Kekulé, *Ann.*, 90, 311 (1854).
330. Karl Keller to General Aniline Wks., U.S. pat. 1,925,191 (1933); 1,949,838 (1934); 1,950,850 (1934)—C.A. 27, 5337; 28, 3260, 3420.
331. Joseph Kenyon, Henry Phillips, Valerie P. Pittman, R. B. Shackleton, Doris E. Kohn, F. H. Yortson, and N. E. Cochinaras, *J. Chem. Soc.*, 1935, 1072–84—C.A. 29, 7272.
332. D. B. Keyes, *Science*, 77, 202–4 (1933)—C.A. 27, 2618.
333. Ernst Keyssner to I.G. Farben., U.S. pat. 2,163,176 (1939)—C.A. 33, 7819.
334. M. S. Kharasch to Du Pont Co., U.S. pat. 2,365,561 (1944)—C.A. 39, 4618.
335. Norman Kharasch and H. R. Williams, *J. Am. Chem. Soc.*, 72, 1843–4 (1950)—C.A. 44, 5854.
336. A. K. Khomenko, *Izvest. Akad. Nauk SSSR Otdel. Khim. Nauk*, 1951, 280–3—C.A. 46, 884.
337. H. Kiemstedt, *Oel. u. Kohle*, 39, 833–6 (1943)—C.A. 38, 5388.
338. H. S. King and F. B. Maddock, *Can. Chem. Process Inds.*, 23, 3–4 (1939)—C.A. 33, 2312.
339. J. A. King and F. H. McMillan, (a) *J. Am. Chem. Soc.*, 68, 632–6 (1946); (b) *ibid.*, 1369–73—C.A. 40, 3423, 5698.
340. Frank Kipnis, Isidore Levy and John Ornfelt, *J. Am. Chem. Soc.*, 71, 2270 (1949)—C.A. 43, 7014.
341. A. I. Kiprianov, Z. P. Suitnikov, and E. D. Suich, *J. Gen. Chem. (USSR)*, 6, 576 (1936)—C.A. 30, 5583.
342. W. R. Kirner and G. H. Richter, *J. Am. Chem. Soc.*, 51, 3131–5 (1929)—C.A. 23, 5472.
343. Jozsef Kiss and Elemér Vinkler, *Acta Univ. Szeged., Chem. et Phys.*, 3, 75–8 (1950)—C.A. 47, 110.
344. Peter Klason, (a) *J. prakt. Chem.*, [2] 15, 193–218 (1877); (b) *Ber.*, 20, 3407–13 (1887).
345. Enrico Knüsli, *Gaz. chim. ital.*, 79, 621–9 (1949)—C.A. 44, 4438.
346. H. P. Koch, *J. Chem. Soc.*, 1949, 387–94—C.A. 43, 7410.
347. J. König and W. Schreiber, *Biochem. Z.*, 184, 105–24 (1927)—C.A. 21, 2340.
348. W. Koerner and G. Monselise, *Gaz. chim. ital.*, 6, 133–42 (1876).
349. K. W. F. Kohlrausch, *Ber.*, 69B, 527–32 (1936)—C.A. 30, 3325.

350. K. W. Kohlrausch and F. Köppl, *Monatsh.*, **63**, 255-70 (1933)—C.A. **28**, 2268.
351. K. W. F. Kohlrausch, A. W. Reitz, and W. Stockmair, *Z. physik. Chem.*, **B32**, 229-36 (1936)—C.A. **30**, 4761.
352. K. W. F. Kohlrausch and H. Wittek, *Monatsh.*, **74**, 1-24 (1941)—C.A. **36**, 6083.
353. I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, **73**, 5118-22 (1951).
354. M. Kondo, *Biochem. Z.*, **136**, 198-202 (1923)—C.A. **17**, 3355.
355. D. R. Koolhaas, *Biochem. Z.*, **230**, 446-50 (1931)—C.A. **25**, 1873.
356. E. Kopp, *Revue scientif.*, **27**, 273; *Ann.*, **64**, 320-1 (1848).
357. Hermann Kopp, *Ann.*, **95**, 307-56 (1855).
358. F. Krafft and R. Schönherr, *Ber.*, **22**, 821-6 (1889).
359. R. L. Kramer and E. E. Reid, *J. Am. Chem. Soc.*, **43**, 880-90 (1921)—C.A. **15**, 1720.
360. C. A. Kraus and E. G. Johnson, *J. Am. Chem. Soc.*, **55**, 3542-7 (1933)—C.A. **27**, 5618.
361. Hermann Krutzsch, *J. prakt. Chem.*, [1] **31**, 1-4 (1844); *Ann.*, **52**, 317-9 (1844).
362. Masaji Kubo, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, **29**, 122-8 (1936)—C.A. **30**, 5847.
363. P. V. Laakso, *Suomen Kemistilehti*, **13B** 8-12 (1940)—C.A. **34**, 5059.
364. A. E. Lacomble to Shell Dev. Co., U.S. pat. 2,009,554 (1935)—C.A. **29**, 6414.
365. K. C. Laughlin to S. O. Dev. Co., U.S. pat. 2,514,300 (1950)—C.A. **44**, 8941.
366. W. T. Lawrence, *Ber.*, **29**, 547-52 (1896).
367. W. A. Lazier and F. K. Signaigo to Du Pont Co., U.S. pat. 2,402,641, 2,402,642 (1946)—C.A. **40**, 5768, 5758.
368. W. A. Lazier, F. K. Signaigo, and J. E. Werntz to Du Pont Co., U.S. pat. 2,402,643 (1946)—C.A. **40**, 5764.
369. W. A. Lazier, F. K. Signaigo, and L. G. Wise to Du Pont Co., U.S. pat. 2,402,645 (1946)—C.A. **40**, 5761.
370. J. M. F. Leaper to National Aniline & Chem. Co., U.S. pat. 1,842,414 (1932)—C.A. **26**, 1618.
371. M. Lecat, (a) "La Tension de vapeur des mélanges de liquides. L'Azéotropisme. Première partie. Données expérimentales. Bibliographie," 1918, Lamertin, Brussels; (b) "Tables Azéotropiques, Tome premier, Azéotropes binaire orthobares." 2nd. Edition, 1949, Uccle, Brussels.

372. H. Z. Lecher and Elizabeth Hardy, *J. Org. Chem.*, **20**, 475–87 (1955).
373. H. Z. Lecher and Kurt Simon, *Ber.*, **55**, 2423–32 (1922)—*C.A.* **17**, 739.
374. W. M. Lee, U.S. pat. 2,020,421 (1935)—*C.A.* **30**, 489.
375. T. A. Lennartz, (a) *Ber.*, **75**, 833 (1942); (b) *Angew. Chem.*, **A59**, 49–55 (1947)—*C.A.* **41**, 5431.
376. Les Consommateurs de pétrole, *Fr. pat.* 891,295 (1944)—*C.A.* **47**, 11254.
377. Rudolf Leuckart, *J. prakt. Chem.*, [2] **41**, 179–224 (1890); *Ger. pat.* 45,120 (1887)—*Ber.*, **21R**, 915 (1888).
378. Rudolf Leuckart and Holtzappel, *J. prakt. Chem.*, [2] **41**, 197 (1890).
379. L. N. Leum and E. R. Birkhimer to Atlantic Refining Co., U.S. pat. 2,309,653 (1943)—*C.A.* **37**, 4240.
380. P. A. Levene and L. A. Mikeska, (a) *Science*, **59**, 158 (1924); (b) *J. Biol. Chem.*, **59**, 473–8 (1924); (c) *ibid.*, **63**, 85–93 (1925); (d) *ibid.*, **65**, 515–8 (1925); (e) *ibid.*, **70**, 365–80 (1926); (f) *ibid.*, **75**, 587–605 (1927); (g) *ibid.*, **84**, 571–99 (1929)—*C.A.* **18**, 1270, 2494; **19**, 1245; **20**, 577; **21**, 521; **22**, 1953; **24**, 1618.
381. P. A. Levene, L. A. Mikeska, and Kurt Passoth, *J. Biol. Chem.*, **88**, 27–59 (1930)—*C.A.* **24**, 5741.
382. P. A. Levene, Alexandre Rothen, and Martin Kuna, *J. Biol. Chem.*, **121**, 747–59 (1937)—*C.A.* **32**, 917.
383. G. R. Levi, *Atti congresso naz. chim. ind.*, **1924**, 373–5—*C.A.* **19**, 1556.
384. G. R. Levi and G. Natta, *Gaz. chim. ital.*, **54**, 973–7 (1924); *Atti acad. Lincei*, **33**, I, 350–3 (1924)—*C.A.* **19**, 2190.
385. T. R. Lewis and S. Archer, *J. Am. Chem. Soc.*, **73**, 2109–13 (1951).
386. H. Ley and B. Arends, *Z. physik. Chem.*, **B15** 311–24 (1932)—*C.A.* **26**, 2120.
387. Justus Liebig, (a) *Ann.*, **11**, 10–4; (b) *ibid.*, 14–18 (1834).
388. A. P. Lien, D. A. McCaulay, and B. L. Evering, *Ind. Eng. Chem.*, **41**, 2698–2702 (1949)—*C.A.* **44**, 2214.
389. R. Linke, *Z. physik. Chem.*, **A187**, 227–34 (1940)—*C.A.*, **35**, 7781.
390. D. J. Loder to DuPont Co., U.S. pat. 2,075,295 (1937)—*C.A.* **31**, 3505.
391. Joseph Loevenich, Hermann Utsch, Paul Moldrickx, and Erich Schaeffer, *Ber.*, **62**, 3084–3104 (1929)—*C.A.* **24**, 1849.

392. O. Loew, *Ärztliches Intelligenzblatt von München* 1879—Quoted by Nencki and Sieber.
393. Carl Löwig and Salomon Weidmann, *Pogg. Ann.*, 49, 123 (1840)—*Ann.*, 36, 321–3 (1840).
394. Anthony Loverde to Hooker Electrochem. Co., U.S. pat. 2,456,588 (1948)—*C.A.* 43, 3460.
395. Arthur Lüttringhaus, H. B. König, and B. Böttcher, *Ann.*, 500, 201–14 (1947)—*C.A.* 43, 1042.
396. V. O. Lukashevich and R. S. Chlenova, *Doklady Akad. Nauk SSSR* 73, 711–4 (1950)—*C.A.* 45, 1565.
397. S. J. Lukasiewicz to Socony-Vac. Oil Co., U.S. pat. 2,515,242, 2,515,927 (1950)—*C.A.* 44, 8958.
398. Eduard Lutter, *Ber.*, 30, 1065–72 (1897).
399. J. P. Lyon, Jr., to Phillips Pet. Co., U.S. pat. 2,435,545 (1948)—*C.A.* 42, 3425.
400. T. F. McCormick and Arthur Lazar to Tide Water Assoc. Oil Co., U.S. pat. 2,263,043 (1941)—*C.A.* 36, 1336.
401. J. P. McCullough, D. W. Scott, H. L. Finke, M. E. Gross, K. D. Williamson, R. E. Pennington, Guy Waddington, and H. M. Huffman, *J. Am. Chem. Soc.*, 74, 2801–4 (1952)—*C.A.* 46, 9405.
402. J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly, and Guy Waddington, *J. Am. Chem. Soc.*, 75, 1818–24 (1953)—*C.A.* 47, 7878.
403. C. Märcker, *Ann.*, 136, 75–95 (1865).
404. Alfonse Mailhe, (a) *Bull. soc. chim.*, (4) 15, 327–9 (1914); (b) *J. usines gas*, 45, 209–12 (1921)—*C.A.* 8, 2674; 15, 3201.
405. Alfonse Mailhe and M. Murat, *Bull. soc. chim.*, (4) 7, 288–91 (1910)—*C.A.* 4, 2297.
406. Alfonse Mailhe and M. Renaudie, *Compt. rend.*, 195, 391–2 (1932)—*C.A.* 26, 5544.
407. W. M. Malisoff, E. M. Marks, and F. G. Hess, *Chem. Rev.*, 7, 493–97 (1930)—*C.A.* 25, 1483.
408. C. Mannich and P. Fresenius, *Arch. Pharm.*, 274, 461–72 (1936)—*C.A.* 31, 1952.
409. J. Marcusson, *Petroleum*, 12, 1149–52 (1917); *Z. angew. Chem.*, 31, II, 62 (1918)—*C.A.* 12, 2435.
410. Maurice Martraire, *Bull. assoc. chim.*, 58, 293–300 (1941)—*C.A.* 36, 4663.
411. C. S. Marvel and P. D. Caesar, (a) *J. Am. Chem. Soc.*, 72, 1033 (1950); (b) *ibid.*, 73, 1097–9 (1950)—*C.A.* 45, 4642; 46, 3016.

412. Simao Mathias, (a) Bols. faculdade filosofia, cienc. letras, Univ. Sao Paulo, 14, Quimica No. 1, 75-140 (1942); (b) Anais acad. brasil. cienc., 18, 23-37 (1946); (c) J. Am. Chem. Soc., 72, 1897-1902 (1950); (d) J. Phys. Chem., 57, 344-6 (1953)—C.A. 40, 2792, 6311; 44, 8185; 47, 6202.
413. L. Mathieu, Bull. assoc. chim. suc. dist., 28, 971-6; Bull. assoc. chim.; Ann. brasserie distillerie, 1911, 329; Wochschr. Brau., 29, 58-60—C.A. 6, 1336, 1651.
414. Jean Maurin and R. A. Pâris, Compt. rend., 232, 2428-30 (1951)—C.A. 45, 8857.
415. E. B. Maxted, Chemistry & Industry, 1938, 759-66—C.A. 32, 8620.
416. F. R. Mayo and Cheves Walling, Chem. Reviews, 27, 387-94 (1940).
417. J. R. Meadow and E. E. Reid, J. Am. Chem. Soc., 56, 2177-80 (1934)—C.A. 29, 797.
418. Louis Médard and François Deguillon, Compt. rend., 203, 1518-20 (1936)—C.A. 31, 1295.
419. B. K. Merezhkovskii, J. Russ. Phys. Chem. Soc., 46, 1082-4 (1914)—C.A. 9, 1899.
420. Fritz Meyer, Ber., 42, 3059 note (1909).
421. K. H. Meyer and W. Hohenemser, Helv. chim. acta, 18, 1061-6 (1935)—C.A. 30, 4047.
422. Victor Meyer, Ber., 19, 3259-66 (1886).
423. Victor Meyer and K. Neure, Ber., 20, 1756-8 (1887).
424. Fritz Micheel and Hans Emde, Ber., 72, 1724-30 (1939)—C.A. 33, 9286.
425. L. A. Mikeska to S. O. Dev. Co., U.S. pat. 2,464,049 (1949)—C.A. 43, 4683.
426. L. W. C. Miles and L. N. Owen, J. Chem. Soc., 1950, 2943-6—C.A. 45, 6158.
427. W. H. Mills and J. B. Whitworth, J. Chem. Soc., 1927, 2738-53—C.A. 22, 785.
428. Yuji Minoura, J. Chem. Soc. Japan, Pure Chem. Sect., 73, 244-6 (1952)—C.A. 46, 6933.
429. J. A. Mitchell, Emil Ott and E. E. Reid, Ind. Eng. Chem., 23, 694-6 (1931)—C.A. 25, 3628.
430. Alwin Mittasch, J. prakt. Chem., [2] 68, 103-4 (1903).
431. H. Mohler and J. Polya, Helv. chim. acta, 19, 1222-39 (1936)—C.A. 31, 1515.
432. J. L. R. Morgan and P. M. Chazal, J. Am. Chem. Soc., 35, 1821-34 (1913)—C.A. 8, 1041.
433. Max Mousseron, Compt. rend., 215, 201-3 (1942)—C.A. 38, 4914.

434. Max Mousseron, H. Bousquet, and G. Marret, *Bull. soc. chim. France*, 1948, 84-90—C.A. 42, 4952.
435. E. Müller and A. Freytag, *J. prakt. Chem.*, [2] 145, 318-20 (1936)—C.A. 30, 5939.
436. E. J. Murphy, *Gas Age*, 84, No. 11, 23-7 (1939)—C.A. 34, 2158.
437. R. C. Murray, *J. Chem. Soc.*, 1933, 739-40—C.A. 27, 4216.
438. L. N. Nakamura, *Biochem. Z.*, 164, 31-3 (1925)—C.A. 20, 1095.
439. S. S. Nametkin and A. S. Sosnina, (a) *J. Applied Chem. (USSR)*, 7, 123-6 (1934); (b) *Doklady Akad. Nauk SSSR.*, 63, 775-8 (1948)—C.A. 28, 7493; 43, 2759.
440. R. Nasini, *Gaz. chim. ital.*, 13, 296-311 (1883); *Ber.*, 15, 2878-92 (1882).
441. G. Natta, *Giorn. chim. ind. applicata*, 8, 367-70 (1926)—C.A. 20, 3273.
442. R. F. Naylor, *J. Chem. Soc.*, 1947, 1532-9—C.A. 43, 999.
443. M. Nencki, (a) *Monatsh.*, 10, 862 (1889); *Ber.*, 34, 201 (1901); (b) *Pharm. C. H.*, 32, 421 (1891); (c) *Arch. exptl. Path. Pharmacol.*, 28, 206-9 (1891)—C. 1891, II, 381; *Ber.*, 25R, 512 (1892).
444. M. Nencki and N. Sieber, *Monatsh.*, 10, 526 (1889); *Sitzber. Akad. Wissen.*, 98, 417-22 (1889).
445. Carl Newberg and F. F. Nord, *Ber.*, 47, 2264-71 (1914); *Biochem. Z.*, 67, 46-50 (1914)—C.A. 8, 3299; 9, 58.
446. Carl Newberg and Erwin Schwenk, *Biochem. Z.*, 71, 118-21 (1915)—C.A. 9, 3058.
447. A. E. Nielsen, *U.S. pat.*, 1,345,220 (1920)—C.A. 14, 2553.
448. F. Niemann, *Archiv. Hygiene*, 19, 117-25, 126-35 (1893).
449. P. S. Nisson and M. R. Mandelbaum to Gray Process Corp., *U.S. pat.* 1,836,183 (1931)—C.A. 26, 995.
450. C. R. Noller and J. J. Gordon, *J. Am. Chem. Soc.*, 55, 1090-4 (1933)—C.A. 27, 1861.
451. F. F. Nord, *Ber.*, 52, 1207-11 (1919)—C.A. 14, 55.
452. N. V. Bataafsche, (a) *Fr. pat.* 804,482 (1936); *Ger. pat.* 681,078 (1939); (b) *Brit. pat.* 532,676 (1941)—C.A. 31, 3507; 36, 1946, 1045.
453. Joseph Obermeyer, *Ber.*, 20, 2918-28 (1887).
454. R. A. Ogg, Jr., *Trans. Faraday Soc.*, 31, 1385-92 (1935)—C.A. 30, 338.
455. J. F. Olin to Sharples Chemicals Inc., *U.S. pat.* 2,527,506 (1950)—C.A. 46, 3070.
456. J. F. Olin and F. B. Dains, *J. Am. Chem. Soc.*, 52, 3322-7 (1930)—C.A. 24, 4766.

457. J. F. Olin and T. E. Deger to Sharples Chemicals, Inc., U.S. pat. 2,349,191 (1944)—C.A. 39, 710.
458. J. F. Olin and J. L. Eaton to Sharples Chemicals Inc., U.S. pat. 2,434,510 (1948)—C.A. 42, 2811.
459. Wolfgang Ostwald, *Kolloid Z.*, 45, 56–82 (1928)—C.A. 22, 4031.
460. Emil Ott to Hercules Powder Co., U.S. pat. 2,034,665, 2,052,210, 2,055,727 (1936); 2,137,584 (1938)—C.A. 30, 2990, 7089, 8245; 33, 1974.
461. Robert Otto, *Ann.*, 143, 100–117 (1867); *J. prakt. Chem.*, [2] 36, 433–51 (1887).
462. Robert Otto, A. Rössing, and J. Tröger, *J. prakt. Chem.*, [2] 47, 94–104 (1893).
463. S. Pagliani, *Ber.*, 11, 155 (1878).
464. L. Palfray, S. Sabetay, and Denise Sontag, *Compt. rend.*, 194, 102–4 (1932)—C.A. 26, 1591.
465. V. C. Parekh and P. C. Guha, *J. Indian Chem. Soc.*, 11, 95–100 (1934)—C.A. 28, 4045.
466. G. S. Parks, S. S. Todd, and W. A. Moore, *J. Am. Chem. Soc.*, 58, 398–401 (1936)—C.A. 30, 4387.
467. J. C. Patrick, Private communication.
468. J. C. Patrick to Thiokol Corp., U.S. pat. 2,479,542 (1949)—C.A. 44, 5377.
469. T. S. Patterson, *Chem. and Ind.*, 43, 196–8 (1924)—C.A. 18, 1110.
470. A. A. Pavlic to Du Pont Co., U.S. pat. 2,467,222 (1949)—C.A. 43, 5418.
471. Pазsche, *J. prakt. Chem.*, [2] 2, 418 (1870).
472. J. Pelouze and August Cahours, *Compt. rend.*, 54, 1242–3 (1862)—*Jahresb.*, 1863, 523–31.
473. F. M. Perkin, *J. Inst. Pet. Tech.*, 3, 227–42 (1917)—C.A. 11, 3424.
474. R. A. Peters, L. A. Stockton, R. H. S. Thompson, F. N. Woodward, A. F. Millidge, and E. J. Gasson to Minister of Supply of the United Kingdom, London, U.S. pat. 2,432,797 (1947)—C.A. 42, 2623.
475. Petri & Stark, *Ger. pat.* 360,608—C.A. 18, 842.
476. Marcel Pexsters, *Bull. chim. soc. Belg.*, 1906, 796–802—C.A. 1, 1970.
477. L. von Pieverling, *Ann.*, 183, 344–59 (1876).
478. P. S. Pinkney to Du Pont Co., U.S. pat. 2,551,813 (1951)—C.A. 45, 9559.

479. Wacław von Piotrowskie, Josef Winkler, and Galicyjskie Towarzystwo Naftowe "Galicia" S. A., Ger. pat. 551,535 (1928)—C.A. 26, 4945.
480. P. S. Pishchimuka, J. Russ. Phys. Chem. Soc., 56, 11-4 (1925); J. chim. Ukraine, 1, 87-9—C.A. 19, 2808; 20, 2816.
481. V. A. Plotnikov, J. Russ. Phys. Chem. Soc., 45, 1162-73 (1913)—C.A. 8, 304.
482. Jakob Pollak, Monatsh., 34, 1673-83 (1913)—C.A. 8, 499.
483. Jakob Pollak, J. von Fiedler, and H. Roth, Monatsh., 39, 179-200 (1918)—C.A. 13, 419.
484. Jakob Pollak, Maria Heimberg-Krauss, Ernst Katscher, and Otto Lustig, Monatsh., 55, 358-78 (1930)—C.A. 24, 4004.
485. C. Porcher and C. Hervieux, Compt. rend. soc. biol., 68, 27-9—C.A. 4, 1761.
486. K. W. Posnansky and Carl Sandvoss to Alexander and Posnansky, Brit. pat. 453,921 (1936)—C.A. 31, 1042.
487. Theodor Posner, Ber., 37, 502-10 (1904).
488. Abbott Pozefsky and N. D. Coggeshall, Anal. Chem., 23, 1611-19 (1951)—C.A. 46, 3857.
489. J. D. Pratt, R. A. Peters, L. A. Stocken, and R. H. S. Thompson, Brit. pat. 579,971 (1946)—C.A. 41, 2077.
490. T. S. Price and D. F. Twiss, (a) J. Chem. Soc., 95, 1725-9 (1909); (b) *ibid.*, 101, 1259-68 (1912)—C.A. 4, 750; 6, 3357.
491. W. C. Price, J. Chem. Phys., 3, 256-9 (1935)—C.A. 29, 4263.
492. W. A. Proell and W. F. Wolff to S. O. Co. of Indiana, U.S. pat. 2,615,786 (1952); Brit. pat. 684,096 (1952)—C.A. 48, 1411, 3991.
493. A. N. Pudovik and N. N. Kudryavtseva, J. Gen. Chem. (USSR), 20, 848-54 (1950)—C.A. 44, 9338.
494. Attilio Purgotti, Gaz. chim. ital., 20, 30 (1890).
495. G. N. Quam and J. A. Wilkinson, J. Am. Chem. Soc., 47, 989-94 (1925)—C.A. 19, 1519.
496. O. R. Quayle and E. E. Royals, J. Am. Chem. Soc., 64, 226-30 (1942)—C.A. 36, 1838.
497. G. Radinger and H. Wittek, Z. physik. Chem., B45, 329-40 (1939)—C.A. 34, 4991.
498. Lina Raffa, Gaz. chim. ital., 69, 14-8 (1939)—C.A. 33, 4191.
499. William Ramsay and John Shields, J. Chem. Soc., 63, 1089-1109 (1893); Z. physik. Chem., 12, 433-75 (1893).

500. H. E. Rasmussen, R. C. Hansford, and A. N. Sachanen, *Ind. Eng. Chem.*, **38**, 376–82 (1946)—C.A. **40**, 3873.
501. F. E. Ray, Mary F. Argus and C. P. Barth, *J. Org. Chem.*, **12**, 794–8 (1947)—C.A. **42**, 1919.
502. P. C. Ray and K. C. Bose-Ray, *Quart. J. Indian Chem. Soc.*, **3**, 75–80 (1926)—C.A. **20**, 3687.
503. P. C. Ray and S. K. Mitra, *J. Indian Chem. Soc.*, **6**, 865–9 (1929)—C.A. **24**, 2108.
504. A. M. Reeves and E. E. Reid, Paper read at Organic Division of Am. Chem. Soc. San Francisco, March 1949.
505. V. Regnault, *Ann.*, **34**, 24–36 (1840).
506. E. E. Reid, (a) *Am. Chem. J.*, **43**, 489–504 (1910)—C.A. **4**, 2270; (b) Personal observation.
507. E. E. Reid and Max Gergel—Unpublished.
508. H. A. Reid, *Proc. Pulp Paper Ind., Tech. Assoc.*, **3**, 479–96, discussion, 496–500 (1949)—C.A. **44**, 8645.
509. A. W. Reitz and W. Stockmair, *Monatsh.*, **67**, 92–103 (1935)—C.A. **30**, 2848.
510. Walter Reppe and Fritz Nicolai to I. G. Farben., U.S. pat. 2,156,095 (1939)—C.A. **33**, 5874.
511. Raymond Reuter and F. L. Gaus, U.S. pat. 2,101,096 (1931)—C.A. **32**, 954.
512. A. Reyckler, *Bull. soc. chim. belg.*, **27**, 110–3 (1913)—C.A. **8**, 1105.
513. S. Reymann, *Ber.*, **7**, 1287–90 (1874).
514. Heinrich Rheinboldt, Martin Dewald, and Otto Diepenbruck, *J. prakt. Chem.*, [2] **130**, 133–46 (1931)—C.A. **25**, 3618.
515. Heinrich Rheinboldt, F. Mott, and E. Motzkus, *J. prakt. Chem.*, [2] **134**, 257–81 (1932)—C.A. **26**, 5544.
516. Heinrich Rheinboldt and Christian Tetsch, *Ber.*, **70**, 675–80 (1937)—C.A. **31**, 4270.
517. E. L. Rinman, *Ger. pat.* 628,799 (1936)—C.A. **30**, 6103.
518. V. M. Rodionov and N. N. Suvorov, *Akad. Nauk SSSR, Inst. Org. Khim. Sintezy Org. Soedinenil Sbornik*, **I**, 10–2 (1950)—C.A. **47**, 8004.
519. H. Roemer, *Ber.*, **6**, 784 (1873).
520. Erich Rosenhauer, Hans Hoffmann, and Walter Heuser, *Ber.*, **62**, 2730–6 (1929)—C.A. **24**, 1381.
521. W. C. J. Ross, *J. Chem. Soc.*, **1950**, 815–8—C.A. **44**, 6838.
522. O. Routala and A. V. Jäättelä, *Cellulosechemie*, **7**, 169–73 (1926)—C.A. **21**, 3127.
523. M. Rubner, *Archiv. Hygiene*, **19**, 136–93 (1893).

524. E. F. Rudakova and A. S. Velikovskii, *Neftyanoe Khoz.*, 25, No. 6, 49–54 (1947)—C.A. 41, 7711.
525. A. Rule, *J. Chem. Soc.*, 99, 558–65 (1911)—C.A. 5, 2374.
526. A. L. Rummelsberg to Hercules Powder Co., U.S. pat. 2,373,343 (1945)—C.A. 40, 607.
527. Horace Russell, Jr., D. W. Osborne, and D. M. Yost, *J. Am. Chem. Soc.*, 64, 165–9 (1942)—C.A. 36, 1542.
528. Paul Sabatier and Alfonse Mailhe, (a) *Compt. rend.*, 150, 823–6, 1569–72 (1910); (b) *ibid.*, 1217–21—C.A. 4, 2094, 2935, 2098.
529. E. Salkowski, (a) *Z. physiol. Chem.*, 8, 417–66 (1883–84); (b) *ibid.*, 89, 485–509 (1914); *Biochem. Z.*, 79, 68–80 (1917)—C.A. 8, 2404; 11, 2224.
530. G. Salomone, *Bol. Laniera*, 43, 992–5 (1929)—C.A. 25, 598.
531. P. L. Salzberg to Du Pont Co., U.S. pat. 2,085,452 (1937)—C.A. 31, 5812.
532. G. Sartori, A. Liberti, and C. Calzolari, *Comite intern. thermodynam. et cinet. electrochim.*, *Compt. rend. reunion*, 1950, 301–4 (Pub. 1951)—C.A. 46, 10011.
533. R. H. Saunders, M. J. Murray, and F. F. Cleveland, *J. Am. Chem. Soc.*, 64, 1230–1 (1942)—C.A. 36, 4028.
534. Alexander Saytzeff and N. Grabowsky, *Ann.*, 175, 348–51 (1875).
535. Martin Schenck and Henry Kirchhof, *Z. physiol. Chem.*, 158, 90–110 (1926)—C.A. 21, 62.
536. Schering-Kahlbaum (Erwin Schwenk and Max Gehrke), *Ger. pat.* 557,247 (1930)—C.A. 27, 374.
537. E. Schirm, R. Hueter, and H. J. Engelbrecht to Deut. Hydrierwerke A.-G., *Ger. pat.* 723,837 (1942)—C.A. 37, 5415.
538. Herman Schlundt, *J. Phys. Chem.*, 5, 503–26 (1901).
539. F. Schmeling, *Braunkohlenarch.*, No. 45, 15–34 (1936)—C.A. 30, 7310.
540. G. G. Schneider, H. Boch, and H. Häusser, *Ber.*, 70, 425–9 (1937)—C.A. 31, 3912.
541. A. Schöberl and E. Ludwig, *Ber.*, 70, 1422–32 (1937)—C.A. 31, 6199.
542. Franz Schütz, *Brennstoff Chem.*, 4, 84 (1923)—C.A. 17, 2775.
543. Franz Schütz, Wilhelm Buschmann, and Heinrich Wissebach, *Ber.*, 56, 1967–75 (1923)—C.A. 18, 581.

544. W. A. Schulze to Phillips Petroleum Co., U.S. pat. 2,392,554, 2,392,555 (1946); 2,426,646, 2,427,309 (1947); 2,502,596 (1950)—C.A. 40, 2349; 42, 585, 406; 44, 5895.
545. W. A. Schulze, J. P. Lyon, Jr., and G. H. Short, Ind. Eng. Chem., 40, 2308-13 (1948)—C.A. 43, 1715.
546. W. A. Schulze, G. H. Short, and W. W. Crouch, Ind. Eng. Chem., 42, 916-21 (1950)—C.A. 44, 11071.
547. Gerold Schwarzenbach, Helv. chim. acta, 15, 1468-81 (1932)—C.A. 27, 1556.
548. Gerold Schwarzenbach and H. Egli, Helv. chim. acta, 17, 1176-82, 1183-96 (1934)—C.A. 29, 1077.
549. Gerold Schwarzenbach and A. Epprecht, Helv. chim. acta, 19, 169-78 (1936)—C.A. 30, 4074.
550. Gerold Schwarzenbach and E. Rudin, Helv. chim. acta, 22, 360-76 (1939)—C.A. 33, 6265.
551. Erwin Schwenk and Max Gehrke to Schering-Kahlbaum, U.S. pat. 2,038,609 (1936)—C.A. 30, 3947.
552. Leon Selitrenny, Monatsh., 10, 908-17 (1889).
553. Sharples Chemicals Inc., (a) Brit. pat. 616,521 (1949); (b) 625,646 (1949)—C.A. 43, 4683; 44, 5377.
554. E. H. Shaw, Jr., and E. E. Reid, J. Am. Chem. Soc., 48, 520-8 (1926)—C.A. 20, 1051.
555. N. Sheppard, Trans. Faraday Soc., 46, 429-39 (1950)—C.A. 44, 9800.
556. P. R. Shildneck and Wallace Windus. Org. Syntheses, 12, 52-3 (1932)—C.A. 26, 3484.
557. D. A. Shirley and J. R. Zeitz, J. Org. Chem., 18, 1591-3 (1953).
558. B. H. Shoemaker and H. R. Batchelder to S. O. Co. of Ind., U.S. pat. 2,211,990 (1940)—C.A. 35, 464.
559. E. C. Shokal to Shell Dev. Co., U.S. pat. 2,633,458 (1953)—C.A. 47, 7826.
560. G. H. Short to Phillips Pet. Co., U.S. pat. 2,610,981 (1952)—C.A. 47, 600.
561. N. Sieber and M. Schoubenko, Arch. Sci. Biol. (St. Petersburg), 1, 315-21 (1892).
562. Hans Siebert, Z. anorg. u. allgem. Chem., 271, 65-75 (1952)—C.A. 47, 4668.
563. Erich Siegfried, Petroleum, 7, 1320-4 (1911).
564. C. Siemens, Ann., 61, 360-2 (1847).
565. F. K. Signaigo to Du Pont Co., (a) U.S. pat. 2,230,390 (1941); (b) 2,402,686 (1946)—C.A. 35, 3266; 40, 5766.
566. S. D. Simpson, Can. J. Research, 25B, 20-7 (1947)—C.A. 41, 3051.

567. B. Singh and R. Singh, *J. Indian Chem. Soc.*, **8**, 209-13 (1931)—C.A. **25**, 5809.
568. Bertil Sjöberg, (a) *Ber.*, **74**, 64-72 (1941); (b) *ibid.*, **75**, 13-29 (1942)—C.A. **35**, 5092; **36**, 6138.
569. Lennart Smith and Bertil Sjöberg, *Ber.*, **69**, 678-80 (1936)—C.A. **30**, 4465.
570. W. V. Smith, *J. Am. Chem. Soc.*, **68**, 2064-9 (1946)—C.A. **41**, 1131.
571. H. R. Snyder and M. E. Chiddix, *J. Am. Chem. Soc.*, **66**, 1002-4 (1944)—C.A. **38**, 3983.
572. Soc. anon. des matières colorantes et produits chimiques de Saint Denis and Robert Lantz, *Fr. pat.* 714,682 (1930)—C.A. **26**, 1617.
573. Socony-Vacuum Laboratories Report.
574. Denise Sontag, *Ann. chim.*, **11**, 1, 359-438 (1934)—C.A. **28**, 4716-8.
575. Q. F. Soper, W. E. Buting, J. E. Cochran, Jr., and Albert Pohland, *J. Am. Chem. Soc.*, **76**, 4109-12 (1944).
576. A. J. Speziale, *Org. Syntheses*, **30**, 35-7 (1950)—C.A. **45**, 116.
577. Louis Spiegler and J. M. Tinker, *J. Am. Chem. Soc.*, **61**, 940-2 (1939)—C.A. **33**, 4187.
578. Georg Spielberger and Otto Bayer to I. G. Farben., *Ger. pat.* 737,334 (1943)—C.A. **38**, 3666.
579. J. M. Sprague and T. B. Johnson, *J. Am. Chem. Soc.*, **59**, 1837-40 (1937).
580. Otto Stadler, *Ber.*, **17**, 2075-81 (1884).
581. S. O. Dev. Co., *Brit. pat.* 602,238, 602,303 (1948)—C.A. **43**, 664; **42**, 8814.
582. Jaroslav Stanek, *Chem. Listy*, **46**, 383-4 (1952)—C.A. **47**, 4296.
583. Hermann Staudinger, G. Rathsam, and R. Kjelsberg, *Helv. chim. acta*, **3**, 853-61 (1920)—C.A. **15**, 518.
584. Hermann Staudinger and Thadeus Reichstein to Intern. Nahrungs-Genussmittel A.-G., *Can. pat.* 283,765 (1928); *U.S. pat.* 1,715,795 (1929); 1,748,527 (1930)—C.A. **22**, 4537; **23**, 3716; **24**, 1869.
585. Norbert Steiger to Roche Products, Ltd., *Brit. pat.* 637,130 (1950)—C.A. **44**, 8380.
586. R. W. Stenzel, *J. Am. Chem. Soc.*, **54**, 870-6 (1932)—C.A. **26**, 2361.
587. M. J. Sterba, *Ind. Eng. Chem.*, **41**, 2680-7 (1949)—C.A. **44**, 2213.
588. H. P. Stevens, *J. Chem. Soc.*, **81**, 79-81 (1902).

589. W. T. Stewart to California Res. Corp., Brit. pat. 629,638 (1949); U.S. pat. 2,510,765 (1950)—C.A. 44, 3514, 7864.
590. Arthur Stoll and Ewald Seebeck, *Helv. chim. acta*, 31, 189–210 (1948)—C.A. 42, 4137.
591. G. G. Stoner and Gregg Dougherty, *J. Am. Chem. Soc.*, 63, 987–8, 1481 (1941)—C.A. 35, 3604, 4365.
592. J. Strakosch, *Gaz. chim. ital.*, 2, 431 (1872).
593. Jan Strating to Hartford Natl. Bank and Trust Co., U.S. pat. 2,549,991 (1951)—C.A. 46, 147.
594. J. Strating and H. J. Backer, *Rec. trav. chim.*, 69, 638–48 (1950)—C.A. 44, 7222.
595. Daniel Strömholm, *Ber.*, 32, 2892–2911 (1899).
596. B. C. Stuer and W. Grob, U.S. pat. 1,421,743 (1922)—C.A. 16, 3093.
597. T. M. Sugden, A. D. Walsh, and W. C. Price, *Nature*, 148, 372–3 (1941)—C.A. 36, 336.
598. S. D. Sumerford to S. O. Dev. Co., U.S. pat. 2,514,299 (1950)—C.A. 44, 8941.
599. A. R. Surrey and H. G. Lindwall, *J. Am. Chem. Soc.*, 62, 1697–8 (1940)—C.A. 34, 6629.
600. Swarts, *Jahresber. Chemie*, 1863—Quoted by Nencki and Sieber.
601. W. Swietoslawski, *J. Russ. Phys. Chem. Soc.*, 40, 1257–1323 (1908); *Z. physik. Chem.*, 65, 513 (1909); *Anzeiger Acad. Wiss. Cracow*, 1909, 941–72—C.A. 3, 637; 5, 1433.
602. Lajos von Szessich to Deut. Gold- u. Silber-Scheideranstalt, U.S. pat. 2,070,961 (1937)—C.A. 31, 2231.
603. F. Taboury, (a) *Bull. soc. chim.*, (3) 29, 761–5 (1903); (b) *ibid.*, 31, 646–52 (1904); (c) *ibid.*, 1183–8; *ibid.*, 33, 836–9, 873 (1905); *ibid.*, 35, 457, 668–74 (1906); (d) *Compt. rend.*, 138, 982 (1904); *Ann. chim. phys.*, [8] 15, 5–66 (1908)—C.A. 2, 3330.
604. M. Tamele, C. J. Ott, K. E. Marple, and G. Hearne, *Ind. Eng. Chem.*, 33, 115–20 (1941)—C.A. 35, 1379.
605. H. G. Tanner to Du Pont Co., U.S. pat. 2,402,694 (1946)—C.A. 40, 5762.
606. D. S. Tarbell and D. K. Fukushima, *Org. Syntheses*, 27, 81–3 (1947)—C.A. 42, 1874.
607. P. O. Tawney to U.S. Rubber Co., U.S. pat. 2,583,975 (1952)—C.A. 46, 9608.
608. D. E. Teets, *J. Am. Chem. Soc.*, 56, 1143–4 (1934)—C.A. 28, 4375.
609. Christian Tetsch, *Dissertation*, Bonn, 1935.

610. V. N. Thatte and A. S. Ganesan, *Phil. Mag.*, **15**, 51–64 (1933)—C.A. 27, 3668.
611. M. D. Thomas, J. O. Ivie, J. N. Abersold, and R. N. Hendricks, *Ind. Eng. Chem., Anal. Ed.*, **15**, 287–90 (1943)—C.A. 37, 2963.
612. H. W. Thompson, *Proc. Roy. Soc.*, **A150**, 603–14 (1935)—C.A. 29, 6503.
613. H. W. Thompson and J. J. Frewing, *Nature*, **135**, 507–8 (1935)—C.A. 29, 3602.
614. H. W. Thompson and J. W. Linnet, *Trans. Faraday Soc.*, **31**, 1743–7 (1935)—C.A. 30, 1624.
615. H. W. Thompson and N. P. Skerrett, *Trans. Faraday Soc.*, **36**, 812–7 (1940)—C.A. 34, 7743.
616. R. B. Thompson, L. W. Druge, and J. A. Chenicek, *Ind. Eng. Chem.*, **41**, 2715–21 (1949)—C.A. 44, 2215.
617. Julius Thomsen, *J. physik. Chem.*, **52**, 343–8 (1905).
618. J. Timmermanns and T. J. F. Mataar, *Bull. soc. chim. Belg.*, **30**, 213–9 (1921)—C.A. 16, 2304.
619. I. N. Tits-Skvortsova, A. I. Leonova, and S. Ya. Levina, *Doklady Akad. Nauk SSSR*, **84**, 741–3 (1952)—C.A. 47, 3247.
620. I. N. Tits-Skvortsova, S. Ya. Levina, A. I. Leonova, and T. A. Danilova, *J. Gen. Chem. (USSR)*, **22**, 135–8 (1952)—C.A. 46, 11120.
621. I. N. Tits-Skvortsova, S. Ya. Levina, A. I. Leonova, and E. A. Karaseva, *Zhur. Obshechi Khim.*, **21**, 242–50 (1951)—C.A. 45, 7514.
622. Masao Tomita and Hiroshi Yamada, *J. Pharm. Soc. Japan*, **71**, 451–2 (1951)—C.A. 46, 992.
623. Masao Tomita, Hiroshi Yamada, and Keiichiro Hozumi, *J. Pharm. Soc. Japan*, **69**, 403–4 (1949)—C.A. 44, 1922.
624. I. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, **1946**, 481–8—C.A. 40, 6988.
625. A. W. Trusty, *Refiner and Natural Gasoline Mfr.*, **10**, No. 7, 91 (1931)—C.A. 26, 3096.
626. I. I. Tsyganok and L. A. Vanyukov, *Vostochnaya Neft*, **1940**, No. 9, 36–8; *Khim. Referat. Zhur.*, **4**, No. 6, 106 (1941)—C.A. 37, 6868.
627. N. B. Tucker and E. E. Reid, *J. Am. Chem. Soc.*, **55**, 775–8 (1933)—C.A. 27, 1322.
628. Tyotaro Tukamoto, *J. Pharm. Soc. Japan*, **59**, 149–68 (1939)—C.A. 33, 4223.

629. R. F. Twist and Samuel Smiles, *J. Chem. Soc.*, 127, 1248–52 (1925)—C.A. 19, 2647.
630. G. G. Urquart, J. W. Gates, Jr., and Ralph Connor, *Org. Syntheses*, 21, 36–8 (1941)—C.A. 35, 6235.
631. Vallin, *Ber.*, 19, 2953 (1886).
632. W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, 7, 472–6 (1942)—C.A. 37, 1083.
633. W. E. Vaughan and F. F. Rust to Shell Dev. Co., U.S. pat. 2,398,481 (1946)—C.A. 40, 3764.
634. S. Vankateswaran, *Indian S. Phys.*, 5, 219–36; *Nature*, 126, 434 (1930)—C.A. 25, 30.
635. G. B. Vespignani, *Gaz. chim. ital.*, 33, I, 73–8 (1903).
636. Tullo Vitali and Mario Nardelli, *Ann. chim. (Rome)*, 41, 499–502 (1951)—C.A. 47, 8443.
637. A. I. Vogel, *J. Chem. Soc.*, 1948, 1820–5—C.A. 43, 2956.
638. Ruth Vogel-Högler, *Acta Phys. Austriaca*, 1, 311–22 (1948)—C.A. 42, 6663.
639. Carl Vogt, *Ann.*, 119, 142–153 (1861).
640. Alexis Voorhies, Jr., and W. M. Smith, *Ind. Eng. Chem.*, 41, 2708–10 (1949)—C.A. 44, 2213.
641. D. Vorländer and Ernst Mittag, *Ber.*, 46, 3450–60 (1913)—C.A. 8, 682.
642. N. N. Vorozhtsov, Jr., and S. N. Mitsengendler, *Compt. rend. acad. sci. (USSR) N.S.*, 1933, 291–4, 294–5; *Russ. pat.* 33,131 (1933); 34,554 (1934); *Org. Chem. Ind. (USSR)*, 2, 457–61 (1936)—C.A. 28, 2340, 4073; 29, 2977; 31, 2181.
643. E. Votocek and V. Vesely, *Ber.*, 47, 1515–9 (1914); *Z. Zuckerind. Böhmen*, 40, 207–11—C.A. 8, 2716; *C. 1916*, I, 602.
644. J. Wagner, (a) *Z. physik. Chem.*, B40, 36–50 (1938); (b) *ibid.*, 439–49—C.A. 32, 6549, 8937.
645. Theodor Wagner-Jauregg and Theodor Lennartz, *Ber.*, 74, 27–32 (1941)—C.A. 35, 2902.
646. P. Walden, (a) *Z. physik. Chem.*, 54, 201 (1906); (b) *ibid.*, 55, 683–720; (c) *ibid.*, 65, 129–225 (1909); 66, 385–444 (1909)—C.A. 3, 976, 2077.
647. P. Walden and R. Swinne, *Z. phys. Chem.*, 79, 716 (1912).
648. W. S. Walls and C. P. Smyth, *J. Chem. Phys.*, 1, 337–40 (1933)—C.A. 27, 3371.
649. Yin Lin Wang, *Z. physik. Chem.*, B45, 323–8 (1940)—C.A. 34, 4626.

650. J. A. Wanklyn and E. Erlenmeyer, *J. Chem. Soc.*, **17**, 190-3 (1864).
651. P. F. Warner to Phillips Pet. Co., U.S. pat. 2,592,089 (1951)—C.A. **46**, 11227.
652. Bengt Weibull, *Arkiv Kemi, Mineral-Geol.*, **23A**, No. 18, 25 p. (1946) (Eng.)—C.A. **44**, 1427.
653. A. F. Wells, *J. Chem. Soc.*, **1949**, 55-67—C.A. **43**, 4910.
654. C. Werner, *Z. f. Chemie*, **1862**, 581—C. **1863**, 203.
655. J. H. Wertz to Du Pont Co., U.S. pat. 2,402,698 (1946)—C.A. **40**, 5765.
656. C. M. Wetherill, *Ann.*, **66**, 117-125 (1848).
657. H. L. Wheeler and H. S. Bristol, *Am. Chem. J.*, **33**, 440-1 (1905).
658. H. L. Wheeler and H. F. Merriam, *Am. Chem. J.*, **29**, 482 (1903).
659. C. R. Wilke, *Chem. Eng. News*, Oct. 4, **1947**, 2896.
660. C. R. Wilke and W. J. Wride, *Ind. Eng. Chem.*, **41**, 395-9 (1949)—C.A. **43**, 3601.
661. C. Willgerodt, (a) *Ber. naturf. Ges. Freiburg*, **8**, 285-302—*Ber.*, **17**, Ref. 3523 (1884); (b) *Ber.*, **18**, 328-31, 331-3 (1885); (c) *ibid.*, **10**, 1686-91 (1877).
662. Dudley Williams, *Phys. Rev.*, **54**, 504-5 (1938)—C.A. **32**, 8935.
663. E. C. Williams and C. C. Allen to Shell Dev. Co., U.S. pat. 2,052,268 (1936); Can. pat. 385,013 (1939)—C.A. **30**, 7122; **34**, 1333.
664. E. C. Williams and C. C. Allen to N. V. Bataafsche, *Brit. pat.* 464,952 (1937)—C.A. **31**, 6673.
665. H. F. Wilson and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 5200-5 (1950)—C.A. **45**, 4214.
666. Wallace Windus and P. R. Shildneck, *Org. Syntheses*, **14**, 54-6 (1934)—C.A. **28**, 2671.
667. D. E. Winkler and S. A. Ballard to Shell Dev. Co., U.S. pat. 2,443,811 (1948)—C.A. **43**, 1062.
668. C. Winssinger, (a) *Bull. Belg. Acad.*, (3) **4**, No. 8 (1882)—*Bull. soc. chim.*, (2) **48**, 109-11 (1887); (b) *Bull. Belg. Acad.*, (3) **14**, 760 (1887)—*Jahresb. 1887*, 1280.
669. W. V. Wirth to Du Pont Co., U.S. pat. 2,395,240 (1946)—C.A. **40**, 3128.
670. H. Wittek, *Monatsh.*, **73**, 231-41 (1941)—C.A. **36**, 5092.
671. R. Witzeck, *J. Gasbeleucht.*, **46**, 21-5, 41-4, 67-73, 84-6, 144-9, 164-9, 185-8—C. **1903**, I, 1052-4.
672. Friedrich Wöhler and J. Dean, *Ann.*, **97**, 1-9 (1856).

673. J. L. Wood and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 2674–81 (1940)—C.A. **34**, 7901.
674. C. C. Woodrow, Marvin Carmack and J. G. Miller, *J. Chem. Phys.*, **19**, 951–4 (1951)—C.A. **46**, 306.
675. Fritz Wrede, *Ger. pat.* 563,875 (1927)—C.A. **27**, 1094.
676. Henri Wruyts, *Bull. soc. chim.*, (4) **5**, 405–12 (1909)—C.A. **4**, 448.
677. Henri Wruyts and G. Cosyns, *Bull. soc. chim.*, (3) **29**, 689–90 (1903).
678. John Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton, *J. Am. Chem. Soc.*, **63**, 1139–41 (1941)—C.A. **35**, 3594.
679. D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257–62 (1940)—C.A. **34**, 3066.
680. V. D. Yasnopol'ski, *Neftyanoe Khoz.*, **26**, No. 7, 51–2 (1948)—C.A. **42**, 9128.
681. Yasuhide Yukawa and Yoshio Kishi, *Mem. Inst. Sci. Ind. Research, Osaka Univ.*, **8**, 163–7 (1951) (in English); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 371–3 (1951)—C.A. **46**, 7061.
682. Yu K. Yur'ev and I. S. Levi, *Doklady Akad. Nauk. SSSR*, **73**, 953–6 (1950)—C.A. **45**, 2934.
683. O. L. Zeide and S. N. Khitrik, *Russ. pat.* 44,552 (1935)—C.A. **32**, 2958.
684. O. Zeise, *J. prakt. Chem.*, [2] **100**, 48 (1919)—C.A. **14**, 1978.
685. W. C. Zeise, *J. prakt. Chem.*, **1**, 257–68, 345–56, 396–413, 457–75 (1834); *Ann.* **11**, 1–10 (1834); *Pogg. Ann.*, **31**, 369–431 (1834); *Ann. chim. phys.*, (2) **56**, 87–96 (1834).
686. W. C. Zeise, (a) *Ann.*, **11**, 1–10 (1834); (b) *J. prakt. Chem.*, **1**, 345–56 (1834).
687. N. Zelinsky and A. Brjuchonenko, *J. Russ. Phys. Chem. Soc.*, **28**, 320 (1896)—*Bull. soc. chim.*, (3) **16**, 1641 (1896).
688. T. Zincke and K. Eismayer, *Ber.*, **51**, 751–67 (1918)—C.A. **13**, 449.
689. T. Zincke and W. Frohneberg, *Ber.*, **42**, 2721–36 (1909)—C.A. **3**, 2577.
690. T. Zincke and P. Jörg, *Ber.*, **43**, 3443–50 (1910)—C.A. **5**, 894.
691. T. Zincke and O. Krüger, *Ber.*, **45**, 3468–79 (1912)—C.A. **7**, 2393.
692. T. Zincke and J. Müller, *Ber.*, **46**, 775–86 (1913)—C.A. **7**, 1720.
693. Helmut Zinner, *Ber.*, **86**, 825–7 (1953)—C.A. **48**, 1263.

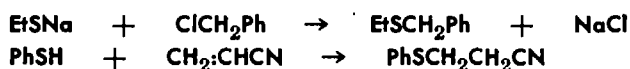
CHAPTER 2.

Reactions of Mercaptans

Introduction

Where the products of a reaction are the subject matter of a later chapter the reaction itself is not considered in this chapter. Examples of such reactions follow.

Two of the methods by which sulfides are prepared are the reaction of a mercaptide and an alkyl halide and the addition of a mercaptan to an unsaturate:



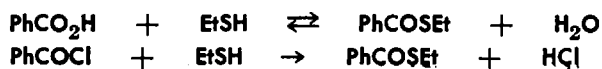
Since both of these will come up in the several chapters on sulfides, they will be omitted here.

Sulfenyl halides are formed by the reaction of a halogen with a mercaptan:



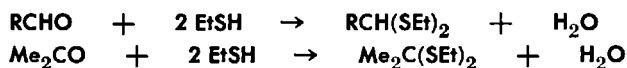
This reaction and its products are to be found in Chapter 3.

The esterification of a mercaptan by an organic acid, or acyl chloride, gives a thioester:



Formally this is an ester of thiobenzoic acid, PhCOSH . Therefore, the esterification of mercaptans is considered in the chapter on thioacids.

Mercaptals and mercaptoles are formed by the reactions of mercaptans with aldehydes and ketones:



These reactions are discussed under thiones and thials.

The formation of disulfides, trisulfides, and tetrasulfides by the reactions of chlorine and sulfur chlorides with mercaptans are mentioned in this chapter, but come up again in the chapter on disulfides.

Mercaptan reactions, not of the classes mentioned, are discussed in this chapter. The chief interest has been in the possible use of most of these reactions for getting rid of the mercaptans that are found in petroleum distillates. In discussing such reactions, the bulk of the space will be given to actual, or proposed, applications for the removal of mercaptans from petroleum distillates. Even then, it is impossible to go into detail. Some articles and patents will be listed.

Of all the classes of sulfur compounds which are found in petroleum distillates, the mercaptans are the worst offenders. Some desulfurization processes have been designed for the sole purpose of eliminating mercaptans, while others have been intended to take care of sulfur compounds in general. As mercaptans are involved in all cases, it seems proper to give brief attention to desulfurization processes in general in this chapter.

Reference is made to some of the innumerable articles on sulfur compounds in petroleum.^{69, 79, 80, 268, 269, 640, 643, 693, 865a, 1002b, 1003, 1023, 1059, 1248a, 1248b, 1260, 1281, 1404a, 1496, 1671a} Special attention is called to a book by Kalichevsky and Stagner⁸⁵⁰ in which desulfurization processes are considered from the standpoint of the gasoline refiner.

The presence of sulfur compounds in gasoline is objectionable^{850, 1450} on account of odor and because they promote gum formation, development of color, corrosion of metals, and the formation of deposits in the engine.^{267, 445c, 449, 516b, 583, 697, 735, 909, 919, 1130, 1424, 1521, 1690, 1728} All sulfur compounds cut down the *lead response* of a gasoline. The worst offenders are the mercaptans

and alkyl disulfides and polysulfides which may be considered as derived from them. The sulfur dioxide from the combustion of the sulfur compounds may cause corrosion in the engine^{443, 444, 822, 1152} and cylinder wear.¹⁷⁰⁴

High-molecular-weight mercaptans must be absent from cable oils.¹¹⁹⁶

In lubricating oils, sulfur compounds may cause deterioration^{1113, 1671b} though it is believed that some of those naturally present are beneficial, acting as antioxidants.^{369, 847, 1153}

The rating of Diesel fuels is raised by the addition of some sulfur compounds,^{845a, 1505} but the wear on the engine increases with the sulfur content.¹¹¹¹ High-sulfur fuel may increase ventilation requirements on account of the oxides of sulfur given off.^{122, 598}

Mercaptans account for only a minor proportion of the sulfur in manufactured gas, but they must be taken care of in its purification.^{9, 76, 221, 547, 617, 619, 747, 757, 776, 777, 787, 790c, 874, 952, 960, 1163, 1198a, 1300, 1343, 1378, 1602}

Reference is made to a number of general articles on the removal of organic sulfur compounds from petroleum distillates.^{11, 141, 144, 180, 260, 262, 417c, 446b, 516a, 516b, 537, 630, 706, 722, 839, 880, 1119, 1322, 1327, 1363, 1422a, 1422b, 1528, 1606c, 1665, 1724, 1725b, 1734, 1761a} Many more articles and hundreds of patents will be mentioned in connection with particular methods.

Formation of Addition Compounds

Ethyl mercaptan unites with water to form the hydrate, $C_2H_5SH \cdot 18H_2O$.^{881b, 1157} This is stable at low temperatures only. An addition compound, $C_2H_5SH \cdot TiCl_4$, has been reported.³⁶⁵ Nitric oxide forms a blood-red addition compound with ethyl mercaptan.^{969b} The same mercaptan forms an addition compound with hydrogen fluoride which dissolves in hydrogen fluoride.⁸⁸³ Primary straight-chain mercaptans can be recovered from such solution unchanged, while benzyl mercaptan is converted to the sulfide, with elimination of hydrogen sulfide.⁹⁵⁶ The combination of mercaptans with hydrogen fluoride may be the basis for the effectiveness of this agent for removing sulfur compounds from hydrocarbons.^{454, 482, 1410, 1428} Or the removal may be due to some catalytic action of the hydrogen fluoride, rather than to its solvent power alone.¹⁰⁷⁵

Boron fluoride also appears to have an affinity for mercaptans.⁵⁷ Its mixtures with hydrogen fluoride have been recommended for the desulfurization of hydrocarbons.^{234e, 780} At -78° boron hydride and methyl mercaptan form an addition compound, $\text{MeSH}\cdot\text{BH}_3$.^{231.5}

Straight chain mercaptans form adducts with urea similar to those of the hydrocarbons.¹⁷⁶⁸

Decomposition of Mercaptans

BY VARIOUS AGENTS

Light seems to split ethyl mercaptan into $\text{EtS}\cdot$ and $\text{H}\cdot$ which end up as ethyl disulfide and hydrogen. The over-all reaction is:¹⁶⁸⁰



The quantum efficiency with respect to hydrogen is less than unity, indicating that there are other reactions. Traces of higher unsaturates and 10% of ethylene are also formed.¹⁰⁷⁸ With methyl mercaptan and the mercury line 2537A, the quantum efficiency is 1.7.¹⁴⁸⁸ In the presence of activated carbon, ultraviolet light changes mercaptan vapors to sulfur-containing condensation products.¹⁰³⁶

X-rays, beta and gamma rays convert a mercaptan, in water solution, to the disulfide. The number of molecules oxidised per ion pair was 3 for x-rays and beta rays and 23% less for gamma rays.⁸⁷ It has been proposed to sweeten naphthas containing mercaptans by exposing them to x-rays and air.¹⁰⁸⁰

Aromatic hydrocarbons may be alkylated by passing them with mercaptans over catalysts.^{1586.3, 1586.5} This may involve the decomposition of the mercaptans; the products are what would be expected from the reactions of the olefins. Tertiary mercaptans, which decompose most readily, are the most efficient.^{493.5}

THERMAL DECOMPOSITION

There have been many investigations of the thermal decomposition of mercaptans, usually with the object of finding conditions under which the mercaptans can be destroyed with a minimum of damage to hydrocarbons that may accompany them. To destroy completely 0.5% of mercaptans, which may be

present in a gasoline, without altering any of the dozens of hydrocarbons, that make up the other 99.5%, is out of the question, but much has been accomplished.

Naturally the start has been made with pure individual mercaptans, without catalysts; other than the walls of the container, but most of the work has been done with catalysts. As the catalyst does not usually change the direction of the decomposition but only its speed, the catalytic and noncatalytic decomposition of mercaptans can be considered together. Many of the scientific articles and practically all of the technical ones are concerned with both kinds. The aim is to convert as much as possible of the sulfur into hydrogen sulfide,

Hydrogen sulfide is split off of a mercaptan at around 300°. ^{1385.5, 1580a, 1593} Branched-chain mercaptans are less stable than their normal isomers. The decomposition into the olefin and hydrogen sulfide appears to be unimolecular. Between 380° and 410°, ethyl mercaptan and ethyl sulfide decompose homogeneously. The rate curves show an induction period, which has been attributed to the formation of an intermediate. No one of ten gases altered the course of the reaction materially. ¹⁶⁰⁴ This explanation has been doubted. ⁹⁰⁵ A tertiary mercaptan, like a tertiary alcohol, goes to the olefin at a moderate temperature. ^{126, 1594.5} Cyclohexyl mercaptan acts more like a tertiary, giving only 12 to 15% of the sulfide, the rest going to cyclohexene. ^{1397, 1598} The decomposition of *n*-propyl mercaptan leads to a pseudo-equilibrium of propylene, hydrogen sulfide, and *i*-propyl mercaptan. ¹⁵⁷⁸

In general, the C-S bond is harder to break than a similarly situated C-O bond. The presence of a carbonyl or cyanogen group or a sulfur atom on a β -carbon weakens the C-S bond just as it does the C-O. The same factors influence the strength of both bonds in the same direction. This subject has been reviewed. ¹⁵⁷⁴

An octyl mercaptan, ⁸⁴⁴ allylic mercaptans, ¹²⁹⁸ and α -thionaphthol, ⁹⁴⁸ go to the sulfides when heated. Mercaptans are converted to alkyl sulfides and hydrogen sulfide by passing their vapors, at elevated temperatures, 300 to 500°, over catalysts, such as sulfides of cadmium, ^{540, 1397, 1454a, 1455} zinc, ^{540, 1454a, 1455} tin, bismuth, aluminum, or iron. ¹⁴⁵⁵ These may be on carriers. Higher-molecular-weight mercaptans and other sulfur compounds may be formed under such conditions. ⁵⁴¹ More or less of the sul-

fide is decomposed to the olefin and hydrogen sulfide. The relative proportions of sulfide and olefin produced depend on the mercaptan and the temperature. Catalyst poisons may be removed by passing the mercaptan over activated carbon.⁷⁷⁸ When passed over a silica-alumina catalyst at 250°, decyl mercaptan gives 30% of decyl sulfide along with decene-1, but at 300° there is no sulfide.¹⁵⁹⁹ Over the same catalyst at 300°, thiophenol^{1598.5} and *m*-dimercaptobenzene go to benzene, thiophenol, and thianthrene.¹⁵⁹⁸ Nickel catalysts decompose mercaptans at 200 to 300°. ^{452, 453, 1570a}

Phosphoric acid is an efficient catalyst for the decomposition of mercaptans.^{53b, 974, 1037, 1044, 1123b} A tertiary mercaptan is split cleanly into olefin and hydrogen sulfide when its vapor is passed, at 300 to 450°, over charcoal impregnated with phosphoric acid.⁷¹

To get information which might apply more closely to petroleum distillates, the pyrolysis of mercaptans, in solution in various hydrocarbons, has been investigated.^{1045a} It has been hoped that conditions could be found under which the mercaptans can be decomposed without too much destruction of the hydrocarbons.^{1580b}

References are given to articles and patents in which the desulfurization of petroleum distillates is the objective and to others in which it is only incidental to cracking. There have been numerous reviews^{83, 516c, 846g, 1370, 1580a, 1626a} and discussions of experimental results.^{191, 257, 314a, 485, 572, 605, 636a, 694, 768, 944, 1361, 1370, 1536} Reference is made to several articles on the nature and treatment of the sulfur compounds that result from cracking.^{89, 445a, 446c, 517, 685, 736, 866, 1092, 1285, 1403, 1507, 1714}

The desulfurization of petroleum by heating,^{2, 439, 442b, 475, 782, 1362b} or by heating with steam, has been claimed.^{114b, 288, 313, 438, 489c, 534, 786, 914, 980, 1106} The addition of various substances to oils is said to aid the decomposition of the mercaptans. Among these are: cresol,¹⁵⁶¹ furfural,^{1025a} terpenes,¹⁵⁰² asphalt,^{941a, 1538} drying oils,^{440a} petroleum residuum,^{1154, 1506} calcium cyanamide,⁹⁴⁷ the sodium addition compounds of anthracene and the like,¹⁴⁵² citrus fruit acids,¹⁷⁰³ and cellulosic materials.^{499b} Ammonium pentachlorodizincate and chloride^{869d} are said to aid decomposition in the vapor phase.

It is impossible to make a sharp distinction between substances that aid the decomposition simply as catalysts and those that

take part in the reactions. Alumina is probably only a catalyst while copper combines with the sulfur. Other additives may function, to a greater or less degree, in both ways.

Many proposals have been made for desulfurizing petroleum distillates by passing their vapors at elevated temperatures over catalysts,^{1246, 1520, 1767b} such as metallic oxides,^{447a, 529c, 529e, 557, 609, 812, 1290, 1544, 1560} ferrous sulfide,^{955, 1295} iron oxide,^{329b, 335b, 529a, 529e, 1046b, 1099, 1304, 1345, 1426, 1427, 1481b, 1486a, 1513, 1558} this with additions,^{53a, 238, 760b, 810, 1123c, 1232, 1352} oxides of molybdenum, nickel,²⁰³ or lead oxide with sodium and aluminum hydroxides,^{333a} alumina,^{760a, 760b, 761, 1215, 1530a, 1725b} silica,^{1725b} alumina with magnesite,^{760b} magnesite alone,^{334, 760b, 761, 1215} sulfides of aluminum,^{1042c} mercury^{1340b} or cadmium,¹²⁷² zirconia,^{1433c} and activated carbon.^{461, 592, 834} Bauxite,^{20, 43, 117, 141, 227b, 413, 470, 615, 634, 638, 644, 678, 684, 723c, 725, 760a, 774, 857, 873, 990, 1134b, 1208, 1259, 1271, 1434, 1436, 1530a, 1690, 1734} fuller's earth,^{20, 40a, 116, 141, 357, 432, 608d, 609, 615, 706, 835, 1134b, 1250, 1275b, 1642, 1651, 1725b, 1761a} clays,^{82, 193c, 306, 442a, 474, 649, 812, 977, 1046a, 1046b, 1061, 1366, 1433b, 1690} and clay with copper or chromium oxide,^{840b} are used in various ways, either with the hot liquid or the vapor. Vapor-phase treatment over clay is especially efficient.^{1450, 1528} Carbon monoxide is mixed with hydrocarbon vapors^{856b} which may be passed over hot alumina.¹⁹⁸ Hydrocarbons are desulfurized by heating them with iron^{292, 335a, 457, 969} or by contacting their vapors with nickel, iron, or cobalt.^{93, 375, 394, 910, 1188, 1570a, 1570b, 1570c, 1707} A pyrophoric metal is effective.^{1379c} Oils may be heated with metals¹⁵⁶⁰ or their vapors passed through metal packing.¹²⁴⁹ They may be distilled from metals,¹²⁷⁶ either molten¹⁶⁷² or emulsified,¹⁰⁶⁸ or their vapors may be passed over a molten metal.^{427, 1354} By the use of a selective silica-alumina catalyst, the sulfur compounds of a distillate may be cracked without much change in the hydrocarbons.⁷⁶⁷ Coal gas is desulfurized over cobalt, iron, or nickel thiomolybdate.^{1071.5}

Oils may be treated with metallic soaps^{132, 386, 529b, 560, 1108} or oil-soluble salts of lead,^{705, 1144} copper, or iron.⁷⁰⁵ A hot oil, or its vapor, with^{351, 1134e} or without hydrogen chloride,^{329a, 691, 927c} is contacted with various metals or their salts. Solutions of salts of various metals have been recommended for treating hydrocarbon vapors.³²²

Aluminum chloride forms complexes with mercaptans and with other sulfur compounds.^{241a, 467, 591, 680, 1460} It splits off hydrogen

sulfide from mercaptans, leaving the alkyl sulfide,³⁷⁶ or some other product.⁹⁴² It causes a tertiary mercaptan to alkylate benzene,¹⁰⁷⁴ but this does not go with a primary.⁹⁴² It has been employed extensively in the treatment of crude petroleums and of distillates. It effects desulfurization along with extensive alterations of the hydrocarbons. It attacks alkyl sulfides and thiophenes as well as mercaptans. Under mild conditions, it may react preferentially with the sulfur compounds. In its use, practice has far outrun theory. Reference is made to a number of articles 131, 141, 535a, 631, 632, 651, 721a, 753, 842, 846b, 1004, 1267, 1404b, 1608, 1727, 1761a, 1761b, 1765 and to some of the patents.^{5, 111, 162a, 220, 352a, 398, 419, 535b, 656, 667, 721b, 781, 837, 843, 928c, 938a, 1005, 1006c, 1009, 1042a, 1254, 1338c, 1469, 1471, 1495, 1512, 1537, 1547, 1564b}

Zinc chloride has been recommended for the desulfurization of petroleum distillates.^{104d, 141, 311, 351c, 352b, 352c, 440b, 447d, 568, 569, 586, 667, 781, 843, 855, 869c, 926, 927b, 928d, 938b, 1136, 1138b, 1166, 1278a, 1468} Zinc hydroxide,¹¹⁶⁵ oxide,^{204, 1134d} sulfate,^{447b, 928a, 1134c, 1660} and zinc ore^{227c, 351a} or silicate^{352d} have been suggested for this purpose.

Several chromium compounds have been recommended for desulfurization.^{227a, 235d, 941b, 1070} Lithium chloride is used with aluminum chloride^{1338b} or silicic acid.^{1338a} Lithium carbonate has been claimed.^{1146b} Chlorides of a number of metals have been suggested.²²⁹

Desulfurization of petroleum distillates may be effected by heating them with lime,^{114a, 124, 247, 292, 327, 717b, 957, 1046b, 1369} distilling them over lime,^{359, 489a, 511, 529d, 712, 1569a} or by passing their vapors over lime.^{90, 244b, 404, 893, 1412, 1530a} Calcium carbonate may be substituted for the lime.^{831, 1120, 1524} A calcium pyrophosphate is claimed.¹⁰⁴⁰

Various catalysts and reactants have been proposed: gravel,⁶⁸¹ granite,⁶⁴⁸ a reforming¹⁷³² or aromatizing^{235e} catalyst, beryllium chloride,^{869b} montmorillonite,³³⁹ boron phosphate,⁹²⁰ magnesium silicate,⁹³³ precipitated silicic acid,⁵⁸⁸ mercuric chloride,^{352c, 447c, 447d} titanium chloride,^{311, 692a} tin dichloride⁸⁴³ and tetrachloride,^{229, 692b} phosphoric anhydride,^{1039b, 1399} this with a metal halide,^{1038, 1039a} a liquid sulfonic acid,^{1025b} sulfuric acid with a metal oxide,^{302b} vanadium oxide,³¹⁶ borax,^{1134a, 1139, 1737} sodium silicate,⁵⁸⁸ sodamide,¹²⁷³ nitrides of various metals,¹⁴¹¹ metallic arsenic,^{405a, 1133a} calcium and magnesium chlorides,^{781, 869a} and potassium hydroxide or carbonate on charcoal.¹³⁸⁴ Sulfitcs or other

reducing agents may be added to an oil during distillation.¹⁴²³

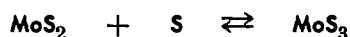
An improved fuel is said to be obtained by adding an organic sulfur compound to an oil, cracking, and desulfurizing.^{309a, 678}

Desulfurization by Hydrogenation

Raney nickel, containing occluded hydrogen, reduces mercaptans and other sulfur compounds, dissolved in absolute alcohol, to the parent hydrocarbons.^{194, 1066, 1508} The sulfur compounds in gasoline are eliminated by this treatment.^{61, 63} Thiophene is desulfurized.⁶⁰¹ Thiophenol and α -thionaphthol, in xylene, go to the sulfides.^{680.5}

Hydrogenation, in the presence of molybdenum sulfide under 300 lb. pressure, converts phenyl mercaptan, in cyclohexane solution, to benzene at 200°. Carbon disulfide goes to methane at 250° and thiophene to butane at 300°. ²⁶⁵ Mercaptans, sulfides, and thiophenes are desulfurized by passing their vapors, with hydrogen, over cobalt molybdate at 440°. ²⁴² The hydrogen is eliminated as hydrogen sulfide. ⁵⁰² Butyl mercaptan, with hydrogen over vanadium oxide, goes to butane and hydrogen sulfide. ⁹⁰² The hydrogenation of methyl mercaptan over nickel sulfide is of the first order with reference to the mercaptan. The rate is lower than with cobalt sulfide. ³²⁶

Various molybdenum compounds have been suggested as catalysts but, regardless of what is put in, the active catalyst appears to be a sulfide. There appears to be an equilibrium:



Hydrogen reduces the trisulfide to the disulfide which then picks up sulfur.⁵⁵³ This conforms perfectly to Sabatier's conception of a catalyst as a carrier, an element which can go up or down from one valency to another, taking up or giving off sulfur. The remarks about molybdenum apply equally to other metals, such as nickel and cobalt. Whether they are put in as metals, oxides, or salts, they are converted to sulfides. Polysulfides of indefinite composition appear to be formed. One author, however, claims better results with oxides than with sulfides.¹¹⁷⁴ Mixed catalysts are common.

The catalytic hydrogenation of petroleum distillates is increasingly important. It is the most thorough way of getting rid, not only of mercaptans, but of all other classes of organic sulfur

compounds. The sulfur is eliminated as hydrogen sulfide. It costs considerably more than other, less efficient desulfurization processes, but there are other substantial benefits which carry a part of the cost.

The hydrogen pressures run from atmospheric to thousands of pounds. The most common temperatures are from 300 to 450°, but higher and lower are mentioned. As catalysts, metal oxides^{402a, 808, 1616} are used. As stated before, these are probably converted to the sulfides.

Several mercaptans, in kerosene solution, were heated 2 hours at 230° in the presence of molybdenum sulfide. The percentages decomposed were: for phenyl mercaptan 94, for ethyl 83, and for *i*-amyl 59%. About 3% of the aliphatic mercaptans were converted to the sulfides, but none of the phenyl.¹¹⁰⁹

Molybdenum compounds are mentioned frequently.^{24, 73, 300a, 300c, 318.5, 319, 377, 644, 759, 789a, 789c, 790a, 791a, 815, 817, 851, 1091, 1109, 1173, 1174, 1198b, 1198c, 1253, 1296, 1297, 1485, 1546, 1603, 1623, 1627b, 1628a, 1628b, 1629, 1630} Cobalt molybdate, or thiomolybdate as it is sometimes called, is a favorite catalyst.^{118, 241b, 241c, 300a, 626, 762.5, 790a, 941b, 1072.5, 1072.7} It is probably more accurate to consider it a mixture of the two sulfides, or polysulfides. Cobalt and compounds of cobalt are frequently mentioned.^{319, 478, 639, 644, 713a, 789a, 789b, 789c, 789d, 1073, 1174, 1461} X-ray examination of the used catalyst shows the presence of cobalt sulfide.^{713b} Tungsten sulfide appears as an alternate, or associate, of molybdenum sulfide.^{73, 195, 300a, 300c, 300d, 301, 319, 377, 759, 789c, 1485, 1603, 1628a} Ruthenium sulfide has been used.^{318.5}

Nickel, the most popular catalyst for ordinary hydrogenations and one that is so easily poisoned by the merest traces of sulfur compounds, becomes an efficient sulfur-insensitive catalyst when it is loaded with sulfur.^{195, 228, 241c, 300a, 300d, 301, 310, 319, 326, 477, 478, 523, 546, 618, 633, 639, 652, 756, 789d, 790b, 791a, 801, 805, 815, 817, 1000, 1001, 1065, 1073, 1173, 1379a, 1461} Nickel, or other metal, may be introduced as a carbonyl.¹⁵⁵

Iron and its oxides are mentioned in many patents as catalysts.^{73, 195, 241c, 300a, 300c, 319, 478, 789b, 801, 814, 1000, 1174, 1379a, 1380, 1448, 1461, 1627a} The vapors may be passed over iron sulfide before hydrogenation.¹⁰⁰¹ Copper,^{73, 195, 319, 478, 639, 713a, 804, 814, 1379a, 1379b, 1498} chromium,^{73, 300c, 319, 564, 789a, 791a, 937, 1174, 1198b, 1623} manganese,^{73, 300c, 319, 814} zinc,^{73, 195, 319, 644, 756, 789a, 814} cadmium,^{1073, 1498}

tin,⁸¹⁴ zirconium,^{241b} titanium,^{241b} thorium,^{241b} aluminum,^{241b} and vanadium^{300c, 1073} compounds are claimed as catalysts.

A cement containing 25%, or more, of alumina, with or without metals, is claimed as a catalyst.⁷ An oil and hydrogen are passed over coke at 330°.²⁵⁸ An oil, hydrogen, and phosgene are contacted with charcoal.^{440c} An oil is heated with aqueous zinc chloride^{440e} or with aluminum chloride^{1006b} in the presence of hydrogen.

The necessary hydrogen may come from the action of steam on metals which may serve also as catalysts.^{786, 1073, 1415} The oil may be passed over a catalyst at a suitably high temperature along with ammonia¹⁶⁴⁰ or a light hydrocarbon³¹⁵ or a hydroaromatic¹³⁷² compound to furnish hydrogen. An oil may be subjected to the simultaneous action of sodium and hydrogen at 300° to effect desulfurization.^{745, 813} The hydrogen may be generated in contact with the oil by the action of steam on the sodium.^{440d}

It has been proposed to desulfurize oils by means of acetylene¹³²⁵ or a metal carbide.^{154, 1007a, 1155}

In the "Platforming" process gasoline and hydrogen are passed over a supported platinum or palladium catalyst. It is claimed that sulfur compounds are converted to hydrogen sulfide almost completely.^{158, 164, 641, 840d, 854} A treatment of this sort was suggested in 1906,^{350a} but only lately has become important.

Hydrogenation by *nascent* hydrogen, generated in various ways, has been suggested.^{61, 63, 630, 683, 1083, 1110, 1123a, 1415, 1588, 1674} The use of atomic hydrogen has been claimed.¹⁵⁹⁴ Several more or less related processes have been proposed.^{353, 790d, 1286, 1605, 1619}

Curiously enough, the hydrogenation may be effected by hydrogen sulfide,^{1379b} which may well be added along with the hydrogen.^{1628a, 1629} In destructive hydrogenation, the presence of sulfur is beneficial.¹⁵⁷¹

Consideration has been given to the thermodynamics of desulfurization by hydrogenation in the presence of metals and their oxides.¹³⁰³

It is well known that coal can be converted to liquid products, hydrocarbons for the most part, by heating with hydrogen at high pressures.¹²⁵ Oils are transformed into lighter oils and gases^{1531b} and are improved by such treatment.^{405b} Distillation residues are

desulfurized.^{886a} Carbon oxysulfide in an oil and hydrogen give hydrogen sulfide.¹⁴⁰⁶ Heating with hydrogen under pressure causes polymerization of unsaturates and of part of the sulfur compounds.⁶⁴² The sulfur is eliminated as hydrogen sulfide.^{1123d}

The hydrogenation of a shale oil without a catalyst gives products containing considerable sulfur, but with a catalyst the sulfur is almost completely removed.¹¹⁷³ Desulfurization of oils is effected if sulfur-resistant catalysts are present.^{123, 216, 300b, 341, 565, 791b, 825, 1206, 1268, 1269, 1649} In one case it is reported that the sulfur content of a distillate from a cracked brown coal tar was reduced from 3.84% to 0.02%.^{1627b, 1630} A shale oil was completely desulfurized.¹¹⁷²

Oxidation

By OXYGEN

The oxidation of a pure mercaptan by air goes on extremely slowly, if at all, but in the presence of a catalyst it may be rapid. Catalysts are not mentioned in the recorded oxidation of benzyl mercaptan,¹⁰³⁴ 4-mercaptobiphenyl,⁵⁵⁰ *p*-nitro-⁸⁴ and *p*-bromophenyl,⁷⁷³ mercaptans and dimercaptomethyl sulfide⁵⁴³ by air, but some may have been present. The most effective catalysts are the copper and iron protoporphyrins; with dithiols the distance between the groups influences the rate.⁸⁸ In fact, all copper and iron compounds speed up the rate of oxidation.⁶⁷⁹ A number of metals and their oxides are claimed as catalysts.^{1199b, 1620}

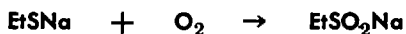
Air may be freed from noxious mercaptans by passing it over such catalysts.^{792c} Gases containing mercaptans are mixed with air and passed over catalysts.^{620, 793a, 809, 1699} Sulfate turpentine can be purified by air oxidation.³⁰⁷

Petroleum distillates are freed from traces of mercaptans by contacting them with various metallic compounds in the presence of air.^{279, 281, 378, 391, 575, 623, 771b, 1135a, 1257}

The oxidation of a mercaptan to the disulfide may be effected by passing its vapor with air over a catalyst, such as bauxite,¹⁰⁸⁸ iron,^{547.5, 1700} copper or other metals,^{547.5} or an alumina-base catalyst.⁷¹⁵ Activated charcoal at 100°, or above, has been recommended.^{104a, 1612} Oxides of nitrogen may be used as oxygen carriers.^{870, 1479, 1480} With their aid, the oxidation may go on to the sulfonic acid.¹²⁹²

In alkaline solution, mercaptans are oxidised by gaseous oxygen.¹⁶⁴³ Ammonium hydroxide may serve as the base.^{1226e} This oxidation can be speeded up by catalysts.^{263b, 497, 824} An organic nitroso compound,^{170d} a substituted phenylenediamine,^{1377.5} *N,N'*-tetrabutyl-*p*-phenylenediamine,^{378.5} and a phenolic compound which can be oxidised to a quinone^{170e} may serve as catalysts. Oxidation is slowed down by hydroquinone^{263b} and by hydrocyanic acid.⁶⁷⁹ The metals that aid the alkaline oxidation, arranged in order, are: arsenic, copper, antimony, zinc, cadmium, silver, iron, and nickel.¹²⁹ The oxidation is aided by supplying the oxygen under pressure.^{503d} It is facilitated by the presence of finely divided solids and by the dispersion of the air in fine bubbles.^{558b, 925} In a solution buffered with sodium bicarbonate, sodium indigodisulfonate is a catalyst for the oxidation.^{497b} Electrolysis in alkaline solution is effective.^{159b, 230, 558a, 559, 1199c} It is claimed that, when hydrocarbons are placed in an electric field, the impurities collect at the electrodes.^{224b}

In a quantitative study, it was found that the rate of oxidation is the faster the more concentrated the alkali. It decreases in the order: propyl, butyl, amyl, benzyl, and phenyl. Somewhat more oxygen than that calculated to produce the disulfide is taken up.¹⁷³⁸ This excess oxygen probably goes to form sodium sulfinate. It is known that dry sodium mercaptide takes up oxygen to form the sulfinate.^{881b}



A lubricating oil is refined by treatment with oxygen in the presence of metallic sodium.¹⁵¹⁹ The above reaction may be involved.

β -Mercaptopropyldimethylamine, $\text{MeCH}(\text{SH})\text{CH}_2\text{NMe}_2$, is oxidised rapidly by air in alkaline solution.¹³⁴² The spontaneous oxidation of β -aminoethyl mercaptan may be attributed to its basicity.⁵⁴⁹

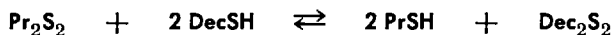
In the petroleum industry, it is common practice to regenerate the alkaline solutions, that have been used to extract mercaptans from distillates, by blowing them with air. The disulfides, which are insoluble in alkali, separate out. This will be taken up later on when alkaline extraction is considered.

The rapid oxidation of mercaptans in alkaline solution by air should be taken into account in making derivatives, such as alkyl sulfides. Sometimes it is stated that "the mercaptan was added

to the alkali dropwise with stirring." This would give excellent opportunity for oxidation which would lead to the contamination of the product with the disulfide. It is better to mix the mercaptan and alkyl halide in a suitable solvent and add the alkali, dropwise if necessary to control the reaction.

BY OXIDISING AGENTS

The simplest case is the conversion of a mercaptan to the disulfide by the disulfide corresponding to another mercaptan. An equilibrium is established:



This reaction is brought about by heating^{23.5, 595} or by the presence of catalysts, sodium hydroxide or mercaptide, or by a halogen acid.⁸⁸⁴

Quinones have been used in the classification of mercaptans as to oxidisability. Several mercaptans are given in the order of decreasing oxidation potential: mercaptobenzothiazole, tertiary mercaptans, such as butyl and dodecyl, primary mercaptans, such as ethyl and butyl, aromatic, such as phenyl and benzyl.^{1071a}

The effectiveness of active oxygen from several sources in decreasing order is: peracids, hydrogen peroxide, hypochlorites, and persulfates. Anodic oxidation is effective.⁷¹⁸ With persulfate, the rate is higher at pH 13 than at pH 10.⁹⁰¹

Oxidation of mercaptans by hydrogen peroxide may give the disulfide,^{47, 56, 109, 464, 1006.5, 1058, 1359} the sulfonic,^{67, 68, 1487} or the sulfuric acid¹⁰⁵⁸ according to conditions.^{750c} A high yield of the sulfonic acid can be obtained from tertiary mercaptans.^{67, 68} β -Aminomercaptans are oxidised to the disulfides.^{86, 1176} The oxidation of thiophenol by benzoyl nitrate is quantitative.⁵²⁰ The use of organic peroxides, or hydroperoxides,^{836c} or of hydrogen peroxide for removing mercaptans from petroleum distillates has been proposed.^{179, 224c, 302a, 718, 1042b, 1258, 1675, 1716a} Sodium perborate in alkaline solution has been recommended.^{1125b} Metal peroxides are said to be useful in the purification of sulfate turpentine.⁹⁷³

Ozone has been suggested as an agent for removing mercaptans from distillates^{30, 224a, 406, 441b, 675, 1051, 1137b, 1557, 1617} and from water.^{1449.}

Nitric acid oxidises mercaptans readily, usually taking them all the way to the sulfonic acids. In many cases, the yields are

nearly theoretical.^{252, 291, 364, 468, 570, 596, 709, 856a, 907, 935, 968, 969b, 1164, 1168, 1244, 1409, 1639, 1693, 1721} Sometimes the optical rotation is reversed.⁹⁵¹ Petroleum distillates have been treated with nitric acid to remove mercaptans.^{528d, 892, 1175a, 1289, 1588, 1589} Nitric acid has been added to oils during distillation.^{528d, 1720}

This is an excellent way to prepare sulfonic acids when the required mercaptans are available. Concentrated nitric acid diluted with 1 or 2 parts of water is put in a flask with reflux condenser. A small portion of the mercaptan is added through the condenser. The onset of the oxidation is shown by the evolution of red fumes. Heat is applied as required. Portions of mercaptan or of nitric acid are added from time to time to keep the reaction going. Care must be taken to avoid an accumulation of *both*, otherwise the reaction may become violent. When the oxidation is judged to be complete, the liquid, which should be clear, is poured into a dish and evaporated on the steam bath to a syrup. To remove nitric acid, water is added and the solution evaporated again. This should be repeated several times. The product is pure enough for many uses. Incomplete oxidation may give the disulfide^{296, 907, 994, 1037, 1226a, 1643} and sometimes the thiosulfonic ester.^{969b, 994, 1242}

Nitrous acid has been recommended for preparing disulfides from mercaptobenzothiazole⁵⁹⁷ and other mercaptans.^{1462.5} Nitrous acid and oxides of nitrogen have been proposed for use in desulfurizing hydrocarbons.^{528d, 889, 1125c, 1289}

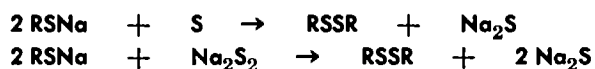
Potassium permanganate oxidises mercaptans to sulfonic acids.^{54, 304, 508, 1195, 1346, 1700} The oxidation potentials of various mercaptans have been determined by permanganate titration.¹³⁹⁶ It has been proposed to purify petroleum distillates by treatment with permanganates,^{393, 688, 1007b, 1128c, 1321, 1541, 1542} manganese dioxide,^{148, 151, 1542} or other manganese compounds.^{410, 528b, 1011}

The oxidation of mercaptans by potassium persulfate is a reaction of the first order with reference to the persulfate. The rate constant is independent of the kind of mercaptan and of its concentration.⁴³¹ It is faster in the presence of an unsaturate.⁹⁰¹ The use of persulfates in the treatment of petroleum distillates has been proposed.^{58a, 688, 1137a}

A variety of other compounds effect the oxidation of mercaptans: chromates,^{304, 448b, 766, 1037} oxides of chromium,^{342, 441c} selenium dioxide,^{1081, 1691} chloropicrin,¹¹⁸⁰ a diazonium compound,¹⁴²⁵ various salts,¹⁶⁷⁸ and nitrosyl chloride.^{838, 940, 1575}

In the presence of alkali, ammonia, or an amine, sulfur converts

a mercaptan to the disulfide.^{103, 750a, 1029, 1219, 1220} This may be supposed to be a reaction of the mercaptide with either sulfur or with sodium polysulfide:



Widely different proportions of the reactants may be used. Extensive use has been made of these reactions in the refining of distillates.^{139a, 141, 234a, 235c, 246, 417b, 503c, 515, 555, 728, 740, 764a, 1060, 1128a, 1145, 1146a, 1324, 1441b, 1525, 1526, 1652}

Ethyl mercaptan and sulfur, in a sealed tube at 150°, give the disulfide and hydrogen sulfide.¹¹⁵⁸ A sour petroleum may be distilled over sulfur.³⁶¹ Conversely, an alkaline solution of the lower mercaptans has been recommended for removing free sulfur from hydrocarbons.¹⁶⁸⁸ This subject will come up again under alkaline extraction and again when the doctor treatment is considered.

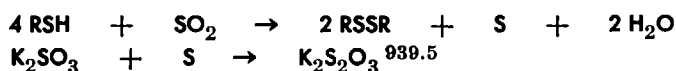
Mercaptans are oxidised to disulfides by ferric compounds. Ferric chloride has been used for the preparation of disulfides^{673, 1771b, 1772, 1773} and this and other iron salts for the sweetening of petroleum distillates.^{107, 308, 311, 590, 687, 781, 792b, 843, 1128b, 1135a, 1186, 1319, 1676} Ferric salts^{26, 575, 1019} or ferric oxide^{251, 329b, 330d, 331, 792d, 1692} may be on adsorbents or mixed with an alkali.^{390b, 996} Bog iron ore has been recommended.¹⁶⁹⁸ A mixture of lime, ferrous sulfate, and sulfur is claimed for the sweetening of gas oil.⁹⁸ Gases are purified by being brought into contact with ferric oxide in aqueous suspension.^{455, 479, 755, 970}

Aromatic mercaptans are converted to disulfides, or polysulfides, by selenium tetrachloride.^{1369.5}

Benzophenone is reduced to tetraphenylglycol, $\text{Ph}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Ph}_2$, by thiophenol, which goes to the disulfide.^{1170.5}

Octadecyl mercaptan catalyzes the transformation of α, α' -azo (ethylbenzene) into phenylmethylketazine. In this the mercaptan appears to give up hydrogen in one stage of the reaction and recapture it in another.^{133.5}

A mercaptan and potassium bisulfite give the disulfide and potassium thiosulfate. This is easier to understand if it is written as two reactions:



Sulfuric acid oxidises mercaptans.¹⁰⁹⁵ The extent of the oxidation naturally depends on conditions, such as concentration of the acid, temperature, and contact. The first product is the disulfide.^{91, 112, 136, 374, 471, 472, 1226c, 1235, 1416} Ethyl trisulfide has been identified as a product, but it must have resulted from a secondary reaction.^{139b} An oxidation product of a disulfide, RSO_2SR , has been reported.¹¹² A mercaptan may be taken all the way to a sulfonic acid.^{149, 1635}

Sulfuric acid has been used extensively in the refining of gasoline and other petroleum products. It is an all-purpose reagent, taking care of all classes of sulfur compounds.^{1725b} It oxidises mercaptans, dissolves out alkyl sulfides, and sulfonates thiophenes. When a gasoline is treated with a simple oxidising agent, the mercaptans, which it may contain, are converted to the disulfides. The odor is improved, but the amount of sulfur present is not diminished. Sulfuric acid dissolves some, or all, of the disulfides which it produces. Butyl disulfide has been recovered from the acid sludge from the treatment of a naphtha. It was accompanied by ethyl, propyl, butyl, and cyclic sulfides.¹⁰²⁴ Methylethyl, methylpropyl, cyclotetramethylene, and cyclopentamethylene sulfides were recovered from a similar sludge.¹⁵⁹⁰ These results show that sulfuric acid acts as a selective solvent for alkyl sulfides. One drawback to the use of sulfuric acid as a refining agent is that it attacks unsaturates and aromatics, of which large amounts are present in modern cracked distillates. This may cause serious losses.

There have been wide variations in the ways of using sulfuric acid for refining distillates. Various strengths of acid from 20% up to fuming and even sulfur trioxide have been recommended. The temperatures of treatment range from below freezing to 200°C. Reference should be made to a number of reviews and discussions.^{91, 112, 139b, 141, 193b, 209, 280, 417c, 445b, 463, 567, 587, 602, 655, 1055, 1095, 1133c, 1167, 1235, 1270, 1387, 1450, 1528, 1577, 1667c, 1669, 1725b, 1727, 1728, 1734, 1761a} Some patents are listed.^{13, 18a, 58b, 59, 147, 350c, 358, 374, 382, 562, 599, 650, 877, 1015, 1020c, 1032, 1124, 1135b, 1181, 1223, 1256, 1278b, 1279, 1289, 1362a, 1532, 1637, 1648, 1679}

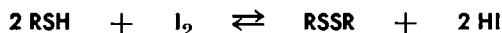
It has been found that the amount of sulfuric acid required is much less and that the sulfating of olefins and sulfonating of aromatics is reduced if the acid treatment is carried on at a low

temperature.^{14, 16, 566, 584, 628a, 885, 1432, 1549} Low temperatures are specified in a number of patents.^{119a, 346, 347, 953a, 954, 998, 1125a, 1230, 1431}

Chlorosulfonic acid also oxidises mercaptans to disulfides.⁹⁴

BY HALOGENS

The simplest case is the conversion of a mercaptan to the disulfide by iodine:



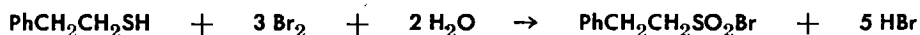
As hydriodic acid is a strong reducing agent, the reaction does not go to completion unless this acid is removed, either by solution in water or by combination with a base.³⁴⁵ This is the neatest way of preparing a pure alkyl disulfide from a mercaptan. The thiol is dissolved in a hydrocarbon, such as benzene, in a flask over water. Iodine is added so long as it is decolorized. The acid goes into the water layer. The benzene solution of the disulfide is separated and fractionated.^{56, 133, 139a, 304, 364, 487, 490, 750c, 773, 859, 882, 1071b, 1429, 1568, 1682, 1694.5} Alkali may be added to take care of the hydriodic acid.¹⁰⁹⁷ In the case of an aminomercaptan, the acid combines with the base and the reaction goes to completion.^{579, 1509, 1510} The titration of mercaptans with iodine is taken up in the analytical section.

With certain mercaptans the sulfenyl iodide, RSI, is formed instead of the disulfide. This will be discussed in Chapter 3.

Bromine in dry carbon tetrachloride converts a mercaptan to the disulfide rapidly and completely.^{56, 490, 770, 1771b} As hydrobromic acid is not a reducing agent, it does not reverse the reaction. With bromine in water, the oxidation goes further:¹⁷⁵⁸



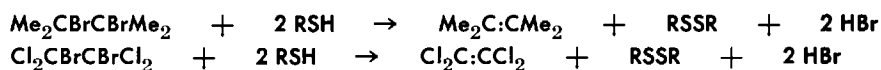
In cold acetic acid, the sulfonyl bromide is formed:^{750d, 1771a}



The addition of bromine to a mixture of two mercaptans gives three disulfides, a mixed disulfide, RSSR', along with the two simple disulfides, RSSR and R'SSR'.¹²²⁷

When an excess of bromine reacts with ethyl mercaptan, in the absence of water, ethyl bromide, sulfur bromide, and hydrogen bromide are produced.⁵³⁶

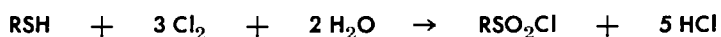
An interesting case is the oxidation of a mercaptan by a dibromide: 1387.5, 1594.7



The liberation of the bromine is due to the crowding.

It has been proposed to add bromine to a cracked distillate and pass the mixture through clay^{992a} or treat it with piperidine.³⁴⁵

Chlorine also converts a mercaptan to the disulfide.⁴⁹⁰ The difficulty is to conduct the reaction in such a way that it will not become violent. In acetic acid,^{1650.5, 1770, 1771b} or in ice water, chlorine oxidises a mercaptan to the sulfone chloride: 282, 395, 1771a



If the temperature is not kept down, the product is the sulfonic acid.

Any compound that gives up chlorine readily can be used instead of free chlorine. Phenyl iodosochloride reacts with a sodium mercaptide: 1763



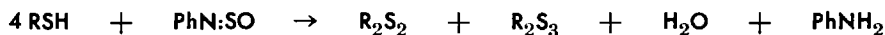
Sulfuryl chloride reacts similarly with either a mercaptan or a sodium mercaptide: 320, 490, 1575



The oxygen of thionyl chloride may also take part in the oxidation: 320, 750a, 750b



Thionylaniline gives similar results: 750b



Phosphorus pentachloride gives up two atoms of chlorine:⁵⁵

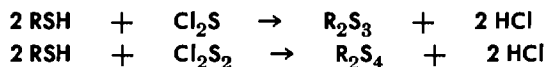


A mercaptan can be converted to the disulfide by a chlorate or a nitrite with hydrochloric acid.^{793b, 1607}

Chlorine has been used in a variety of ways to sweeten petroleum distillates.^{159a, 205, 222, 274, 328d, 345, 399, 489b, 491, 552a, 733, 771a, 772, 788, 934, 992a, 1006a, 1006c, 1087, 1184, 1216, 1252b, 1302, 1492, 1501, 1576, 1579, 1659}

Chlorine, in the form of hypochlorites, usually sodium or calcium and sometimes those of other metals, has been recommended for the removal of mercaptans and other sulfur compounds. Occasionally chlorine and water or hypochlorous acid have been used. There are numerous articles ^{44, 138, 140, 141, 165, 193a, 232, 417a, 421, 424, 466, 537, 593a, 630, 706, 726, 846d, 1063, 1069, 1084, 1301, 1528, 1665, 1666, 1700, 1725b, 1726, 1734, 1759, 1767a, 1775} and patents on various ways of using hypochlorites in petroleum refining. ^{22a, 22b, 45, 162b, 163, 174, 206, 210, 244a, 303, 366, 416, 418, 420, 448d, 489b, 528c, 552b, 606, 607, 611, 716, 792a, 833, 927a, 930, 993, 1006a, 1006c, 1087, 1132, 1137c, 1187, 1231, 1252a, 1252b, 1284, 1337, 1381, 1407, 1420, 1441a, 1492, 1514, 1564a, 1569b, 1576, 1582, 1591, 1592, 1675} When a petroleum distillate containing various sulfur compounds is treated with a hypochlorite, probably many different reactions go on but, unless the treatment is not too vigorous, the mercaptans are converted to disulfides which remain in the oil.¹⁷²⁷ Oxidation by a chlorite has been recommended.^{796c} Oxidation by hypochlorite in the presence of amines leads to condensation products.⁴⁸

The reactions of mercaptans with sulfur chlorides may be classed as oxidations, since hydrogen is removed from the mercaptan. However, the products are not always disulfides. They may be trisulfides ²⁹³ or tetrasulfides: ^{750a, 881b, 1238}

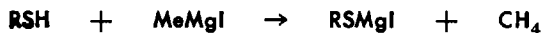


It must be remembered that chlorine-sulfur and sulfur-sulfur bonds are labile and that the sulfur chlorides are statistical compounds. The alkyl polysulfides, obtained from them, are mixtures, though their compositions may approximate trisulfides or tetrasulfides. This will be considered more fully in the chapter on disulfides. The use of sulfur chloride in refining hydrocarbons has been proposed.^{1239a}

Formation of Mercaptides

The most characteristic reaction of mercaptans, as Zeise recognized, is the formation of mercaptides.

By the Zerevitinov method, a mercaptan shows the presence of one active hydrogen.^{711, 1766}



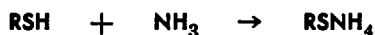
Similar reactions take place with the alkyl compounds of aluminum, zinc, cadmium, lead, boron, mercury, and bismuth.¹¹⁸² Sodium naphthalene reacts slowly.¹⁴⁵²

Zeise found that hydrogen is evolved and a solid formed when potassium metal is added to mercaptan. He recognized the product as one in which a hydrogen atom had been replaced by a metal.^{1764a, 1764b, 1764c}

The inactivation of metal hydrogenation catalysts by mercaptans may be attributed to the formation of mercaptides. This effect varies with the length of the alkyl chain.¹⁰⁷²

AMMONIUM MERCAPTIDES

When a mercaptan is added to liquid ammonia a mercaptide is formed:



This reacts with sodium:¹⁷⁰⁸



Since ammonia is a weak base and mercaptans are feeble acids, ammonium mercaptides are unstable and hydrolyze instantly on contact with water. Thus the presence of water must be avoided if it is desired to separate mercaptans from hydrocarbons by means of these salts.^{1376a} In dioxane solution, thiophenol forms salts with amines.⁶²¹

In order to eliminate mercaptans and other sulfur compounds from petroleum products, it has been proposed to heat them with ammonia to the temperature at which ammonia begins to dissociate.^{991, 992b, 1028, 1248a, 1641} An oil may be heated with ammonia under pressure, in the presence of a catalyst,^{287, 897} with ammonia and ammonium persulfate,²⁸⁷ or with ammonia and steam.⁵³² The ammonia may serve as a source of hydrogen rather than as a base.

ALKALI MERCAPTIDES

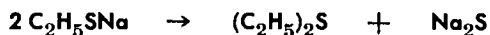
When 25% aqueous sodium hydroxide is saturated with methyl mercaptan, the mercaptide, $\text{CH}_3\text{SNa} \cdot 4.5\text{H}_2\text{O}$, separates out as long flat needles, readily soluble in water and in alcohol. Its water solution gives off mercaptan only slowly on boiling.¹²⁶⁵

Sodium ethyl mercaptide, EtSNa , is left as a voluminous white powder when sodium is added to an ether solution of the mercaptan and the ether evaporated. It is hydrolyzed instantly by water.^{881a, 881b}

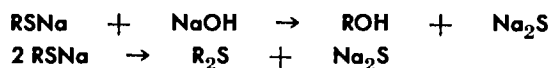
When a 50% sodium hydroxide solution is agitated with a concentrated hydrocarbon solution of a mercaptan having eight or less carbon atoms, the sodium mercaptide separates and may be filtered off.^{402b} A sodium mercaptide may be made by the action of sodium on a mercaptan in an inert medium,⁴⁷³ or on an alkyl disulfide in liquid ammonia¹⁷⁰⁶ or in ether.¹¹⁴⁷

As sodium reacts with mercaptans, its use for removing them from petroleum distillates seems logical. At high temperatures it reacts also with some hydrocarbons.³¹² It has been proposed to refine petroleum products by treating them with sodium in various ways.^{253, 254, 255, 332, 362, 369, 469, 492b, 496, 499a, 719, 743b, 775, 888, 1035, 1126d, 1142, 1393, 1554, 1563, 1586b, 1650, 1653a, 1653b, 1705} Other alkali metals are claimed in several of these patents. Calcium,^{332, 1126d} barium, and magnesium³³² are mentioned also.

Dry sodium mercaptide is decomposed above 200° :^{881b}



The stabilities of a number of sodium mercaptides have been compared. The mercaptans were added to excess of 3 *N* sodium hydroxide solution and heated to 260° for 2 hours. Two reactions may take place:



The percentages decomposed are shown in Table 1.2.

TABLE 1.2

Mercaptan	Et	Pr	Bu	<i>i</i> -Bu	Am	Hex	Hep
Total Decomposition	55.4	52.2	49.6	36.2	42.9	37.0	35.0
To R_2S	11.0	12.1	8.1	6.1	9.9	3.1	10.4
● Secondary							
Mercaptan	<i>i</i> -Pr	<i>s</i> -Bu	<i>s</i> -Am	<i>s</i> -Hex	<i>s</i> -Hep		
Total Decomposition	65.4	59.1	56.0	48.8	47.0		
To R_2S	5.2	2.6	6.3	3.6	15.3		

The total decomposition is greater with secondary than with primary. The longer the carbon chain, the more stable is the mercaptide. It is possible that the higher mercaptans were not entirely in solution.¹³⁵

β -Phenylethyl mercaptan is split into styrene and hydrogen sulfide by potassium hydroxide at above 200° but the α -isomer is only slightly affected. γ -Phenylpropyl mercaptan is partly decomposed.^{1229, 1517}

Thiophenol is taken out of an oil by contacting with fused potassium hydroxide.⁸ Dodecyl mercaptan is converted to lauric acid by this treatment.^{81, 1202d, 1205.5}

An early patent for purifying naphthas by heating with sodium hydroxide solution was granted in 1866.¹⁴⁹⁰ A still earlier patent¹⁸⁶³ claimed the deodorizing of oil residuum with sodium hydroxide.¹¹⁰⁴ There have been many recent patents on modifications of this process.^{152, 927d, 971, 1016, 1245, 1464, 1523} Alkali may be added during the distillation of a petroleum.^{119b, 236, 284, 371, 442c, 1086, 1112, 1150} Hydrocarbon vapors may be brought into contact with sodium hydroxide or other alkali.^{19a, 193c, 390a, 1126a, 1261, 1323, 1367, 1374, 1695} This may be done counter-current-wise.^{971a, 871, 872} Terpenes may be freed from mercaptans by treatment with alkali.¹²⁸⁷ High-boiling mineral oils are purified by a caustic alkali wash.^{690a}

Solid sodium hydroxide is effective in removing mercaptans.^{233a, 1477, 1761b} In the substantial absence of water, sodium and potassium hydroxides remove mercaptans and sulfur from hydrocarbons.^{19b, 145, 379, 848, 1526, 1632, 1709, 1710, 1761b} For taking thionaphthalene out of naphthalene, dry alkali and a high temperature are desirable.¹⁶⁸³ The alkali may be used in an anhydrous solvent.^{1201a} The particles of alkali may be of colloidal dimensions.⁸⁴⁹ A naphtha and molten caustic may be passed through a colloid mill.

A suspension of magnesium hydroxide has been proposed.⁵⁵⁶

Removal of Mercaptans by Alkaline Extraction

This subject has been ably reviewed.^{846f} The use of lead tetraethyl to raise the octane number of gasolines has brought about a radical change in the methods of dealing with mercaptans. Formerly they were objectionable only on account of odor and corrosion. The "sour" gasoline was "sweetened" by converting the

mercaptans into disulfides. The odor was improved and corrosion diminished, but the actual sulfur content remained the same. Mercaptans counteract the beneficial effect of lead tetraethyl. The disulfides are even worse in this respect.^{142, 193b, 512, 668, 689, 704, 748, 846a, 875, 903, 911, 943, 964, 1316, 1356, 1437, 1606a, 1622, 1690, 1717, 1746} Mathematical relationships between the amounts of different classes of disulfides and the lowering of octane rating have been worked out.^{6, 963, 1395} Disulfides are also antagonistic to antioxidants^{1748a} and cause instability in gasolines.^{120b} Therefore, it is necessary to remove mercaptans from the gasoline instead of oxidising them to disulfides.^{1725b}

Alkaline extraction has to do with mercaptans and with them only. It has been studied scientifically and quantitative measurements have shown just what can be done and how to do it. This information has been applied to practice on a huge scale. Within the last few years, the importance of mercaptans has diminished since smaller quantities of them are produced in present day catalytic cracking.

The solubility of mercaptans in aqueous alkali was one of the first properties noted by their discoverer, Zeise. Early makers of mercaptans recommended separating them from by-product sulfides by solution in aqueous sodium hydroxide from which they were subsequently liberated. Fermentation gave huge quantities of ethanol and by-product fusel oil supplied generous laboratory quantities of *n*-propyl, *i*-butyl and *i*-amyl alcohols. Most investigations were based on these starting materials. The mercaptans corresponding to these alcohols are soluble in aqueous alkali. When it became desirable to take mercaptans out of petroleum distillates, it was natural to try extraction with aqueous alkali. It was found that ethyl, *i*-propyl and *i*-butyl mercaptans can be taken out by this means.^{139a} Fortunately the chief mercaptans present in petroleum distillates are the lower ones from butyl on down.

When it comes to the higher mercaptans, extraction with aqueous alkali becomes progressively less efficient. The mercaptans are acidic but weakly so. Values of the dissociation constant, *K*, for several mercaptans¹⁷³² are given in Table 2.2. Assuming 2×10^{-11} for the higher normal mercaptans,¹⁷³⁹ calculation shows that in 1 *N* aqueous sodium hydroxide, the concentration of the ionized portion of the mercaptan is two thousand times

that of the unionized. Thus the total amount of a mercaptan that can be dissolved by 1 liter of 1 *N* alkali is to be found by multiplying the solubility in water by 2000. The data are in Table 2.2. The solubilities of the mercaptans in aqueous alkali fall off rapidly. Above nonyl, they would be very low.

TABLE 2.2
*Solubilities of Some Mercaptans in Water and in
1 N NaOH Solution*
(grams per liter)

Mercaptan	$K \times 10^{11}$	In water	In 1 <i>N</i> NaOH
Methyl	—	23.30	very soluble
Ethyl	2.52	6.76	very soluble
Propyl	2.26	1.96	very soluble
Butyl	2.21	0.57	very soluble
Amyl	2.00	0.164	328.0
Hexyl	(2)	0.047	94.0
Heptyl	(2)	0.0138	27.6
Octyl	(2)	0.0040	8.0
Nonyl	(2)	0.00115	2.3

If there is a hydrocarbon layer in contact with an aqueous solution of alkali, any mercaptan that may be present will be partitioned between the two. Naturally the same equilibrium will be established regardless of whether the mercaptan was originally in the hydrocarbon or in the aqueous layer. There have been several investigations of partition coefficients and from them the extent of removal of a given mercaptan by a specific treatment can be calculated.^{325, 682, 918, 1618, 1739} Since a mercaptan is only partially removed by one extraction, successive treatments are required. Many plant designs and operating methods have been described.^{2, 10c, 28, 29, 32, 41, 46, 50, 104f, 235b, 263b, 273, 415, 492a, 574, 671a, 749, 840c, 1027, 1121c, 1247, 1318, 1320, 1368, 1371b, 1433a, 1450, 1518, 1530d, 1717, 1734, 1750c}

The extent of the removal of a mercaptan is influenced somewhat by the nature of the hydrocarbon but depends chiefly on the nature and molecular weight of the mercaptan. Measurements have been made of the extraction by aqueous sodium hydroxide of several mercaptans from naphtha, containing amounts of mer-

captans equivalent to 0.05 to 0.08% of sulfur.^{178, 181} Some of the results are in Table 3.2.

TABLE 3.2

*Extraction of Several Mercaptans from a Naphtha
by Different Strengths of Alkali*

Mercaptan	0.76 N NaOH %	2.18 N %	2.92 N %	6.06 N %
<i>n</i> -Butyl	62	83	78	69
<i>s</i> -Butyl	56	76	75	63
<i>n</i> -Hexyl	12	26	18	18
<i>s</i> -Hexyl	10	17	14	10
<i>n</i> -Nonyl	11	13	11	11
<i>s</i> -Nonyl	6.2	10	6.2	6.2

In another investigation, the extractions were: ^{417b, 417c}

	%		%		%
Ethyl	97.1	<i>i</i> -Propyl	87.2	<i>i</i> -Butyl	62.8
<i>n</i> -Propyl	88.8	<i>n</i> -Butyl	63.2	<i>i</i> -Amyl	33.0

In the extractions given in Table 3.2 the amount of sodium hydroxide was twenty to two hundred times that required by the mercaptans. The 2.18 *N* alkali removed more of the mercaptans than either the weaker or stronger alkali. Other investigators have found that there is no advantage in using alkali stronger than 2 *N*.^{1094, 1739} Apparently the mercaptan is salted out by the strong alkali. It has been proposed to treat hydrocarbons with alkali under such conditions that three layers will be formed: the hydrocarbon, the caustic alkali solution, and the alkali mercaptide.^{1745c}

It is to be noted in Table 3.2 that less of the secondary mercaptans is taken out than of the isomeric primary. The secondary are more soluble in water but are weaker acids.

Exact determinations have been made on the extraction of methyl mercaptan from a butane-butene mixture and of ethyl from a pentane-pentene mixture.³²⁵ The results are in Table 4.2. The "ratio" is the mercaptan in the aqueous layer divided by that in an equal volume of the hydrocarbon layer. The chief interest here is in the effect of a large or small excess of alkali.

TABLE 4.2

Extraction of Mercaptans by 2.2 N NaOH Solution
(The figures are in grams of sulfur per liter)

	Original	After extraction	In NaOH	Ratio	% RSH extracted	% NaOH neutralized
MeSH	13.20	0.018	13.8	733	99.86	19
	21.60	0.036	21.56	600	99.84	30
	38.40	0.089	38.31	432	99.77	54
MeSH	54.30	0.264	54.04	205	99.52	77
	59.80	0.443	59.36	134	99.26	84
EtSH	10.61	0.069	10.54	153	99.35	15
	28.40	0.223	28.18	126	99.21	40
	42.70	0.501	42.20	84	98.83	60
	57.50	1.160	56.34	49	97.98	79

The figures show that the extraction of these mercaptans is practically complete, even when there is only about 20% excess of the alkali.

The partition of mercaptans between benzene and water and sodium hydroxide solutions at 25° has been studied. The concentrations of mercaptans were 0.1 to 0.5 *N*, corresponding to 0.4 to 2.0% of sulfur. The amounts of the lower mercaptans taken out were equivalent to 50 to 80% of the alkali. The percentages are those of the total mercaptan found in the aqueous layer. The results are in Table 5.2^{45b} and are plotted in Figure 1.2, curves I and II.

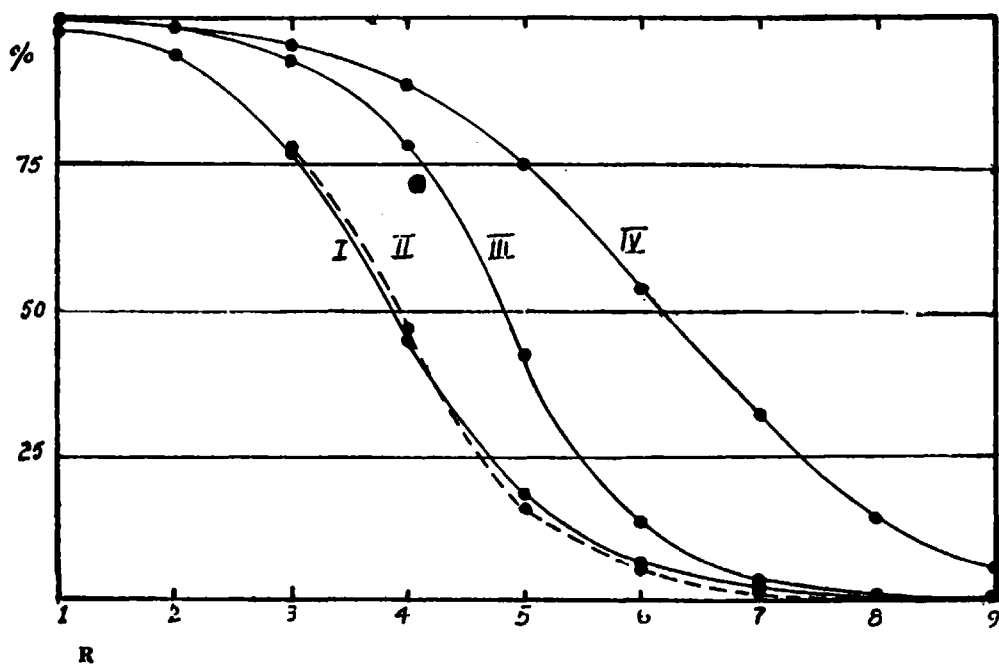
TABLE 5.2

*Percentages of Mercaptans Taken out of Benzene
by Aqueous Sodium Hydroxide*

NaOH	0	0.225	0.626	1.69
Methyl	5.65	97.1	97.9	—
Ethyl	2.14	89.0	94.0	—
<i>n</i> -Propyl	0.32	64.0	77.0	—
<i>i</i> -Propyl	0.42	67.0	78.0	—
<i>n</i> -Butyl	0.077	32.0	47.0	—
<i>s</i> -Butyl	0.121	29.0	45.0	—
<i>n</i> -Amyl	0.021	10.1	18.4	28.0

TABLE 5.2 (Continued)

NaOH	0	0.225	0.626	1.69
<i>s</i> -Amyl	0.027	8.4	16.0	25.0
<i>n</i> -Hexyl	0.0070	—	6.3	15.0
<i>s</i> -Hexyl	0.0083	—	5.3	8.5
<i>n</i> -Heptyl	—	—	1.8	2.8
<i>s</i> -Heptyl	—	—	1.3	1.90
<i>n</i> -Octyl	—	—	0.50	0.72
<i>s</i> -Octyl	—	—	0.35	0.45
<i>n</i> -Nonyl	—	—	0.21	0.26
<i>s</i> -Nonyl	—	—	0.16	0.14

FIGURE 1.2. *Partition of Mercaptans between Hydrocarbons and Aqueous Sodium Hydroxide with or without Methanol*

Curve I. Extraction of Primary Mercaptans from Benzene by 0.626 N NaOH

Curve II. The Same for Secondary Mercaptans

Curve III. Extraction of Primary Mercaptans from Isooctane by 0.5 N NaOH

Curve IV. The Same with 50% Methanol

For methyl mercaptan, the extraction is nearly complete with the weakest alkali which was in only slight excess. The stronger alkali took out only 0.26% of the *n*-nonyl. Any secondary mer-

captan is more soluble than the corresponding primary but, with the exception of isopropyl, is more difficult to extract. The greater acidity of the primary more than compensates for its lower solubility. This was noted in Table 3.2.

The nature of the hydrocarbon has some effect. The results of extraction from three hydrocarbons are shown in Table 6.2.^{458b}

TABLE 6.2
Percentage of Mercaptans Extracted by 0.42 N Sodium Hydroxide

	Benzene	<i>n</i> -Heptane	Cyclohexane
Ethyl	93.70	97.30	97.60
<i>n</i> -Amyl	13.90	21.70	21.90
<i>s</i> -Amyl	12.30	17.20	19.00
<i>n</i> -Octyl	0.32	1.07	0.43
<i>s</i> -Octyl	0.23	0.72	0.20

The extraction from the nonaromatic hydrocarbons is better than from benzene.

Similar experiments have been made, using isooctane (2,2,4-trimethylpentane) as a solvent for the mercaptans.¹⁷³⁹ The results are in Table 7.2.

TABLE 7.2
Extraction of Mercaptans from Isooctane with 0.5 N Aqueous Sodium Hydroxide at 20° and with Water

Mercaptan	Water	0.5 N NaOH
Methyl	8.400	99.70
Ethyl	4.250	98.70
<i>n</i> -Propyl	0.990	93.00
<i>n</i> -Butyl	0.220	78.10
<i>t</i> -Butyl	0.380	71.00
<i>n</i> -Amyl	0.052	42.40
<i>t</i> -Amyl	0.071	26.60
<i>n</i> -Hexyl	0.012	13.70
<i>n</i> -Heptyl	0.0026	3.20
<i>n</i> -Octyl	0.0006	0.72
<i>n</i> -Nonyl	—	0.15

In the introduction to Table 2.2 it was shown that the solubilities of the higher mercaptans in 1 *N* sodium hydroxide are approximately 2000 times as great as in water. In Table 7.2 it is seen that 0.5 *N* alkali extracts 1230 times as much heptyl mercaptan from isooctane as does pure water. For octyl mercaptan this ratio is 1200. These figures are in reasonable agreement. The tertiary mercaptans are more soluble in water than the primary but are less acidic.

Since the solubility of mercaptans in water increases as the temperature is lowered, extraction is improved. In Table 8.2 are the results of extracting *n*-butyl mercaptan from isooctane with water and with 0.5 *N* sodium hydroxide.¹⁷³⁹

TABLE 8.2

*Extraction of n-Butyl Mercaptan from Isooctane
at Different Temperatures*

°C	Water	0.5 <i>N</i> NaOH
0	0.245	88.2
20	0.230	78.2
25	0.225	73.6
40	0.215	63.5

Taking the figures of Table 5.2 for 0.626 *N* alkali, the effects of successive extractions can be calculated (see Table 9.2).

TABLE 9.2

*Percentages Remaining in Benzene after Several Extractions
with 0.626 *N* Alkali*

Mercaptan	1	2	3	4	5
Methyl	2.1	0.044	0.009	0.0002	—
Ethyl	6.0	0.360	0.021	0.00	—
<i>n</i> -Propyl	23.0	5.290	1.220	0.28	0.06
<i>i</i> -Propyl	22.0	4.840	1.060	0.23	0.05
<i>n</i> -Butyl	53.0	28.100	14.900	7.90	4.20
<i>s</i> -Butyl	55.0	30.200	16.600	9.10	5.00
<i>n</i> -Amyl	81.6	67.000	54.000	44.00	36.00

TABLE 9.2 (Continued)

Mercaptan	1	2	3	4	5
<i>s</i> -Amyl	84.0	71.000	59.000	50.00	42.00
<i>n</i> -Hexyl	93.7	88.000	82.000	77.00	71.00
<i>s</i> -Hexyl	94.7	90.000	85.000	79.00	76.00
<i>n</i> -Heptyl	98.2	96.000	95.000	93.00	91.00
<i>s</i> -Heptyl	98.7	97.000	96.000	95.00	94.00

Extraction from nonaromatic hydrocarbons would be somewhat better, but it is obvious that the extraction of the higher mercaptans is impracticable.

An alkaline salt, such as tripotassium phosphate,^{1200a, 1376b, 1552c} and quaternary ammonium^{1200b, 1744, 1745a} and tertiary sulfonium^{1200c, 1745b} bases have been recommended instead of the alkali.

By extracting in two stages, first with a solution of an organic base, or weak alkali, and later with a strongly alkaline solution, strongly acidic compounds and mercaptans can be taken out separately.^{235b, 1375, 1729} Individual mercaptans may be taken out of hydrocarbons by selective absorption.^{323a}

Solutizers

Emphasis has been put on the fact that the difficulty of extracting mercaptans by an aqueous alkali wash is due to their slight solubility in water and to their low acidity. Nothing can be done to raise their acidity, but their solubility in the aqueous layer can be increased by the addition of various substances. Anything that has this effect is called a "solutizer." It is frequently observed that the solubility of an organic compound in water is greatly diminished by the presence of salt or other inorganic substance. Thus propanol may be "salted out" of its aqueous solution by the addition of potassium carbonate. Conversely, the solubility of a mercaptan in water may be increased by the presence of water-soluble organic compounds.

The effect of the addition of methanol to water and to 0.5 *N* sodium hydroxide on the extraction of mercaptans is shown in Table 10.2. Some of the figures are quoted from Yabroff and

White and some are calculated from their data, others are extrapolated.¹⁷⁴⁹

TABLE 10.2

Extraction of Mercaptans from Isooctane by 50% Methanol, by 0.5 N Sodium Hydroxide, and by 0.5 N Alkali in 50% Methanol

Methanol NaOH	50% 0	0 0.5 N	50% 0.5 N	Improvement %
Methyl	24.10	99.7	99.3	—
Ethyl	11.30	98.7	98.7	—
<i>n</i> -Propyl	4.39	93.1	95.3	2.3
<i>n</i> -Butyl	1.77	78.1	88.7	13.5
<i>t</i> -Butyl	2.47	71.0	81.3	14.5
<i>n</i> -Amyl	0.73	42.4	75.0	78.0
<i>t</i> -Amyl	1.05	26.6	49.1	85.0
<i>n</i> -Hexyl	0.30	13.7	53.8	290.0
<i>n</i> -Heptyl	0.134	3.2	32.1	900.0
<i>n</i> -Octyl	0.039	0.72	14.0	1840.0
<i>n</i> -Nonyl	0.019	0.15	5.7	3700.0

The extraction of methyl and ethyl is so good with aqueous alkali that there is scarcely room for improvement, but with the higher mercaptans the effect is great. These results are plotted in Figure 7, curves III and IV.

Almost any water-soluble organic substance added to aqueous alkali will serve as a solutizer and assist in the extraction of mercaptans. To be useful as a solutizer, any proposed compound must meet certain requirements. Obviously it must be stable in a high concentration of alkali, not only at low temperatures but also at high, when the mercaptans are driven out by steaming. It must not be extracted by the hydrocarbons from which the mercaptans are to be removed. Methanol meets these requirements, but has the disadvantage that it is volatile and goes over with the mercaptans. However, it can be recovered and put back in the alkali.

There has been much interest in solutizers.^{176e, 193b, 259b, 887, 978, 1204b, 1747, 1750d, 1751c} Methanol has received much attention.^{100b, 143, 201, 219, 402c, 498, 696, 1017, 1041a, 1067} The "Unisol" process is based on it.^{115, 218, 518, 985, 1119, 1690}

Many substances have been claimed as solutizers, lower alcohols,^{1018, 1041d} ethylene,^{1751e} propylene,^{1724b} butylene,^{1741a} and trimethylene,^{1742d} glycols, diglycols,^{1742c} polyethylene glycols,^{1750e} alkyl glycols,^{1742e} monoethers of several glycols,^{1740a} diamines, alkanolamines, diaminoalcohols, aminoglycols, other amines,^{501a, 1203, 1240e, 1740c, 1741b} and nitroparaffins.^{836b} It has been proposed to use salts of the lower aliphatic acids,^{259a, 323b, 1204a, 1553a, 1750a, 1751a} of naphthenic acids,^{65a, 166, 349, 1030, 1553a} of phenylacetic acid,^{1201b, 1752a} of acid oils,¹⁰³¹ of dicarboxylic acids,^{1752e} of hydroxyacids,^{1751b} of aminoacids,^{4d, 1751d} of cumic acid,^{1221b} of ether-acids,^{4a} of sulfide-acids,^{4b, 1280} of thiophosphoric^{121a} and of sulfonic acids.^{1202b, 1553a} Halogen substituted acids, which are subsequently hydrolyzed, may be put in.^{698c, 1398} Salts of phenols or cresols, alone^{116, 214, 698a, 700, 723d, 1202c, 1553b, 1752c} or mixed with those of aliphatic acids^{170a, 1750b, 1752d} or of thiophenols,^{698a} may also be used. Salts of naphthenic acids may be combined with cresols,^{170c, 698b} with Cellosolve,^{65b} or with glycols or amines.^{65a} Tar acids,^{17, 62, 1028} wood tars,¹²¹² anisol,²⁸³ and polyhydroxybiphenyl^{698e} have been mentioned. The reaction products of alkali with shellac,¹⁷¹ copal,⁶⁴ rosin,^{699, 1553c} and yacca gum⁷⁰² are said to be useful. Tannic acid, with or without oxygen, is an important solutizer.^{548, 929, 987, 1214, 1614b} Emulsion breakers are useful with solutizers.^{75, 343, 1191a, 1193}

Potassium isobutyrate has been specially recommended.^{166, 175, 176c, 259c, 263c, 1743, 1746, 1748a, 1749} The usual solution is 3 *N* potassium isobutyrate and 6 *N* potassium hydroxide. As this contains 378 g. of the salt and 336 g. of the alkali in 1 liter of solution not much room is left for the water. The peculiar thing about isobutyric acid is that its alkali salts are not salted out by the high concentration of alkali. The natural oxidation inhibitors, which are supposed to be alkylated phenols, are removed by the isobutyrate solutizer but not by the mixed isobutyrate-alkylphenate.^{1748b} These natural inhibitors may be returned to the oil.^{542a}

A solutizer may be added to the alkaline solution with which hydrocarbon vapors are contacted for the removal of mercaptans.^{1202a}

Phenols and other weakly acidic substances, as well as mercaptans, can be removed from nonmiscible solvents by alkaline extraction.^{1750c}

So far solutizers were discussed that are intentionally put into the alkaline wash liquors. Actually considerable amounts of solutizers are acquired by these liquors in the course of the extractions. Naphthenic acids, alkylphenols, and other acidic compounds which may be present in the naphthas pass into the alkaline solution and serve as solutizers.^{698d} The sodium mercaptides from the solution of the lower mercaptans serve as solutizers for the higher mercaptans.⁹⁶¹

Solutions of alkali in methanol or ethanol or a mixture of alcohols have been recommended.^{99, 104e, 276, 1201a, 1251, 1305b, 1371a, 1713} As the solubilities of the undissociated mercaptans in such solvents are high, the extractions are complete. The disadvantages in their use are the cost and the difficulty of recovery and reconditioning the solvent for reuse.

Regeneration of Wash Liquors

Regeneration of the spent wash liquor is essential to economic operation. The mercaptans that have been taken up must be removed so that the wash liquor can be reused. This may be accomplished in three ways: steaming out, oxidation to disulfides, and extraction.

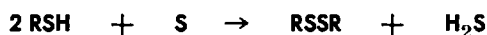
Earlier in this section, it was pointed out that a considerable proportion of the mercaptan is present in the molecular form along with its ions in alkaline solution. This must be in equilibrium with its vapor above the solution. With rise in temperature, the solubility of a mercaptan in water decreases while its vapor pressure increases. If the vapor above the solution is removed, some of the undissociated mercaptan will evaporate to restore the equilibrium. This causes some of the dissociated mercaptan to revert to the undissociated form. If the vapor is continuously removed, all of the mercaptan will eventually pass out of the solution. Mercaptans, provided they are reasonably volatile at 100°, can be steam distilled out of even strongly alkaline solution. Curiously enough methyl, which is the lowest boiling, goes over more slowly than those for some distance above it. At 100° the vapor pressure of hexyl mercaptan is 150 mm., of heptyl 70 mm., and of octyl 30 mm. All of these and those below them go over with steam at good rates. Above nonyl, the vapor pressures at 100° are too low, but the amount of these higher mercaptans is negligible.

Advantage is taken of these facts for the regeneration of alka-

line solutions that have been used for the extraction of mercaptans. The extraction is effected at a low temperature at which the solubility of a mercaptan is high and its vapor pressure low. The mercaptans are then steam-distilled out. Steam distillation is applicable whether or not a solutizer is present. A volatile solutizer goes over with the mercaptans and must be separated from them in a special operation. A few references are given without going into details.^{10c, 28, 32, 85, 139a, 176a, 176c, 176d, 239, 542b, 704, 723b, 949, 950, 1041b, 1082, 1202a, 1470, 1555, 1742f, 1752b, 1753} It is desirable to remove emulsifiers before steam-distilling.^{176b, 1033, 1192} Any hydrocarbons that have been dissolved along with the mercaptans will go over also.^{1205e}

As extraction is a reversible process, it has been proposed to extract the mercaptans from the alkaline wash by kerosene or other suitable solvent.^{211, 263a, 373, 724b, 1191b}

A method of regeneration that is used extensively is the oxidation of the mercaptans to the disulfides which are not soluble in the alkaline solution and can be separated from it. The oxidation may be effected by blowing with air.^{273, 497, 1740b, 1742a, 1745e} Some oxidation takes place spontaneously when steam distillation is used.^{417b} The oxidation may be facilitated by catalysts.^{4c, 169, 170b, 172, 283c, 689c, 1204c, 1375, 1465, 1466} Oxidation may be effected by oxygen at an elevated temperature and under pressure,^{690b, 1530d} or by a compound containing active chlorine.^{1433a} The spent liquor may be washed with a hydrocarbon containing sulfur:



The disulfide is taken up by a hydrocarbon.^{235a, 779a, 1529}

Various impurities accumulate which must be eliminated.^{701, 1201c, 1711} Methods of analysis are available.^{853, 906}

There is the possibility of recovering enormous quantities of mercaptans from the spent liquors.¹⁷⁰⁰ As industry develops, uses will doubtless be found for these or for products that may be made from them.

The alkaline solution which has been used for extracting mercaptans may be treated with chloracetic acid to make sulfide acids, RSCH_2COOH .^{886b}

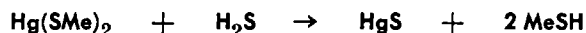
HEAVY-METAL MERCAPTIDES

One of the first things that Zeise noted about his new compound, ethyl mercaptan, was its ability to form insoluble pre-

precipitates when it was added to solutions of salts of the heavy metals. He made sodium, potassium, platinum, mercury, gold, copper, silver, and lead mercaptides.^{1764a, 1764b, 1764c, 1764d} Vogt reported sodium, lead, copper, mercury and silver mercaptides.¹⁶⁴³ Klason prepared mercaptides of thallium, iron, nickel, cobalt, zinc, cadmium, mercury, tin, platinum, and bismuth.^{881a, 881b} Human made the *i*-butyl mercaptides of potassium, mercury, lead, copper, and gold.⁷⁸⁴ Löwig and Weidmann used ethylene mercaptan for making mercaptides of the heavy metals.^{969a, 969b} Mercury derivatives of methyl,¹²¹¹ propyl,¹³⁶⁵ and *t*-butyl³⁸⁸ mercaptans were early preparations.

Mercaptides have been prepared from the mercaptan and oxides of gold, silver, and lead, but the usual way is to add the mercaptan to an aqueous solution of a salt of the metal.^{77, 708, 921, 1661, 1764a, 1764b, 1764c, 1764d} The mercaptides of the heavy metals are so insoluble in water that they precipitate immediately. However, the acid liberated from the salt must not be allowed to accumulate, else the reaction will not be complete. Ammonia, or other base, should be added so as to keep the *pH* just below 7. For the higher mercaptans, which are insoluble in water, alcoholic solutions are convenient. The precipitated mercaptide is filtered off. It is well to wash it with water containing some of the mercaptan to prevent hydrolysis. All mercaptides of metals are decomposed by strong hydrochloric acid into metal chlorides and free mercaptans.^{881d} Heavy-metal mercaptides of *o*-aminothiophenol are prepared by the addition of solutions of the salts to a solution of its hydrochloride.¹⁵³⁴

Although the mercaptides of the heavy metals are very slightly soluble in water, the corresponding sulfides are still less so. Therefore, the mercaptan is liberated and the sulfide precipitated when hydrogen sulfide is passed into a water suspension of the mercaptide: ^{1264, 1764a, 1764c}



It has been proposed to convert the mercaptans in a petroleum distillate into heavy metal mercaptides from which the naphtha may be distilled.^{1108, 1207}

Mercury

Mercuric mercaptides are most characteristic and have been relied upon for the isolation and identification of mercaptans.

They are readily prepared by precipitation from mercuric salts or by treating mercuric oxide with the mercaptan.^{612.5, 614, 739, 862.5} Shaking a solution of a disulfide with mercury gives the mercaptide.^{904, 939a}

Mercury mercaptides can be recrystallized from organic solvents and many of them have satisfactory melting points. A number of these are given in Table 11.2 in the section on the identification of mercaptans.

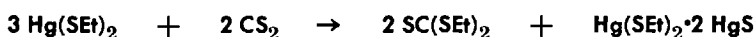
The ethyl mercaptide is monoclinic and the propyl, amyl, hexyl and heptyl mercaptides are isomorphous with it, while the octyl is triclinic and the butyl is tetragonal.¹⁶⁸⁴

With mercuric ions, cysteine and reduced glutathione give three mercaptides each, according to conditions.^{1555.5}

The mercaptans in petroleum fractions have been isolated and identified by converting them into the mercury derivatives.^{538, 1175b} At 180 to 190°, these mercaptides decompose into mercury and the disulfide: 401, 939a, 1226d, 1764d



A mercuric mercaptide reacts with carbon disulfide to form a trithiocarbonate and a complex: ¹⁴⁰¹



Mercuric benzyl mercaptide, in benzene solution, is decomposed by ultraviolet light into mercury, mercuric sulfide, and benzyl disulfide. In sensitivity to light, the mercury mercaptides are in this order: benzyl > *n*-propyl > *i*-propyl > *t*-butyl > phenyl.^{862.5}

Phenylmercury and phenyl mercaptan, heated together, give mercury, phenyl disulfide, mercury phenyl mercaptide, and benzene.^{909.5}

Under certain conditions the half mercaptides, EtSHgBr, MeSHgCl, EtSHgI, AmSHgCl, PrCH(Me)SHgCl, Et₂CHSHgCl, DecSHgCl and DodSHgCl, are precipitated.^{130, 153, 384, 741b, 820, 828b, 1311c} These may be formed from the mercaptide and mercuric chloride.^{750c} There is an equilibrium:

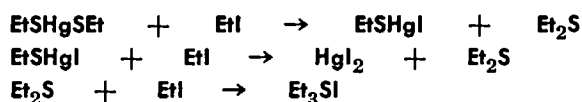


The ethyl and phenyl compounds, EtSHgCl and PhSHgCl, are formed when ethyl and phenyl thioacetates are treated with mercuric acetate and then with sodium chloride.^{1400, 1401.5}

Albumin, which contains a mercaptan group, precipitates the half mercaptide, ASHgCl , from mercuric chloride solution.^{437.5}

EtSHgCl does not melt at 260° but PrSHgCl melts at 182° . These form addition products with mercuric chloride: $\text{EtSHgCl} \cdot \text{HgCl}_2$, m. 151° and $\text{PrSHgCl} \cdot \text{HgCl}_2$, m. 139° .²⁷⁰ X-ray studies have been made of these.^{828a} Similar compounds from mercuric nitrite are known: RSHgNO_2 and $(\cdot\text{CH}_2\text{SHgNO}_2)_2$.^{1311a, 1314} Ethylmercaptomercury acetate, EtSHgOAc , nitrate, EtSHgNO_3 , carbonate, $(\text{EtSHg})_2\text{CO}_3$, and benzoate, $\text{PhCO}_2\text{HgSEt}$, have been reported.¹⁴⁰⁰ Derivatives of mercaptosulfonic acids will be discussed in Chapter 4.

A mercury mercaptide may react with an alkyl halide:

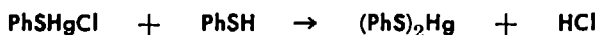


The sulfonium iodides form double salts with mercuric iodide, $\text{Me}_3\text{SI} \cdot \text{HgI}_2$, and $\text{Et}_3\text{SI} \cdot \text{HgI}_2$.^{741a, 741b}

Dissolved in ethyl acetate, phenyl mercury mercaptide reacts with mercuric chloride:



This is reconverted to the mercaptide by phenyl mercaptan:



It decomposes when heated:^{939b}



Mercury derivatives have been prepared from thioborneol.^{186, 673, 1736}

An alkylmercury hydrosulfide, RHgSH , has been claimed as a fungicide and insecticide.^{426a} Mercury methyl mercaptide is a catalyst for the addition of methyl mercaptan to allyl alcohol.⁸⁵²

Many complicated compounds have been reported from mercuric mercaptides with mercury salts and alkyl halides. The alkyl mercapto-mercuric nitrites, RSHgNO_2 , react with alkyl iodides to form such compounds as $\text{Me}_2\text{S}_2\text{HgI}_2\text{MeI}$, m. 162° , $\text{Et}_2\text{S}_2\text{HgI}_2\text{EtI}$, m. 112° , $\text{Et}_2\text{S}_2\text{HgI}_2\text{MeI}$, m. 86° , $\text{MeEtS}_2\text{HgI}_2\text{EtI}$, m. 67° , $\text{MePrS}_2\text{HgI}_2\text{PrI}$, $\text{MeBuS}_2\text{HgI}_2\text{BuI}$ and even more complicated ones.^{1311a, 1311b, 1314} Ethylmercaptomercuric bromide reacts with iodoform to give $2 (\text{EtS})_2\text{Hg} \cdot \text{HCl}_3$, m. 85.5° .⁸²⁰

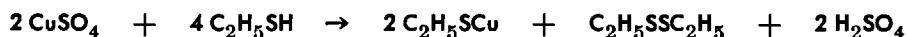
Ethylmercury ethyl mercaptide, EtHgSEt , from EtHgCl and EtSH , is a yellow oil, m. -3 to 0° , which can be distilled *in vacuo*. The mixed mercaptide, EtHgSPh , melts at 61° .¹⁴⁰²

Phenylmercury aryl mercaptides have been prepared from phenylmercury and *p*-chlorophenylmercury chlorides and the aryl mercaptans. The melting points of PhHgSAr and $\text{ClC}_6\text{H}_4\text{HgSAr}$ are: phenyl 103.5° , 140° ; *o*-tolyl 169° , 141° ; *p*-tolyl 104° , 145° ; benzyl 135° , 130° ; α -naphthyl 154.5° . . .^{1571.5}

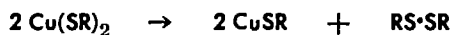
Mercaptans can be removed from distillates by contacting them with solutions of mercuric chloride,^{861, 1305a, 1344} or acetate,¹⁷⁸ with mercuric oxide^{390c} or with metallic mercury^{1116, 1149a} or amalgam.^{1149a, 1149b} Methyl mercaptan can be taken out of gases by a 3% solution of mercuric chloride.¹¹⁸³

Copper

Copper mercaptide was supposed to be the cupric compound, $(\text{C}_2\text{H}_5\text{S})_2\text{Cu}$, until Klason showed that the reaction product of a mercaptan with a cupric salt is a cuprous mercaptide mixed with the disulfide: ^{881d}



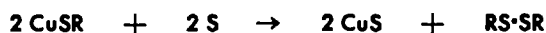
It is curious that this seems to have been overlooked by a number of chemists who still write formulae for cupric mercaptides. This reaction offers a convenient method for the estimation of mercaptans in hydrocarbons which will be discussed in the analytical section. It has been suggested that unstable cupric mercaptides are the first products. If so, they decompose quickly: ⁸⁹⁵



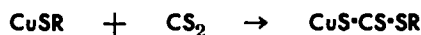
Cuprous mercaptides have been prepared, from primary and secondary mercaptans up to nonyl, by shaking an aqueous solution of copper acetate with a benzene solution of the mercaptan.⁴¹² The cuprous derivatives of the normal primary and of *i*-propyl and *s*-butyl mercaptans are insoluble in benzene, or in ether, but those of the higher secondary are soluble.

When a naphtha containing a mercaptan is treated with copper acetate and then steam-distilled, it comes over "sweet" and brings with it the disulfide, if this is sufficiently volatile. The amount of this may correspond to from one half to two thirds of the original mercaptan. The disulfides from the higher mercaptans are scarcely volatile with steam.^{183, 185}

A cuprous mercaptide reacts with sulfur: ¹⁴⁸⁹



More sulfur may be taken up to form the trisulfide.¹²³⁸ It combines with carbon disulfide to make a trithiocarbonate: ⁴¹²



Cupric sulfide reacts with a mercaptan in benzene solution:



As the cuprous mercaptides that are formed from the primary and lower secondary mercaptans are insoluble in the hydrocarbon they remain on the surface of the copper sulfide while those from the higher secondary go into solution. It is remarkable that such an insoluble substance as copper sulfide should be dissolved by a mercaptan. As this takes place in hydrocarbon solution the reaction is probably not ionic.¹⁴⁸⁹ Amorphous copper sulfide is said to be effective in removing sulfur compounds from hydrocarbons.⁶¹²

It is known that a mercaptan and hydrogen cyanide corrode copper rapidly.¹¹⁶³ Copper powder reacts with a mercaptan, probably with the aid of the oxygen of the air: ^{387a, 387b}



In two experiments, the disulfide formed was equivalent to 47 and 48% of the mercaptan that disappeared.¹⁷²⁸

Cuprous mercaptides from sulfurized terpenes are claimed as additive agents for lubricating oils.^{519, 908}

Copper and copper compounds have been used extensively for desulfurizing petroleum distillates.^{10d, 387a, 387b, 743a, 846e, 1438b, 1725a}

An early desulfurization method was the Frasch process. This attained considerable importance and has been described in a number of articles.^{69, 141, 156, 271, 527, 706, 865b, 1248b, 1351, 1486a, 1727} The first of twenty Frasch patents, U.S. 378,246, Feb. 21, 1888, was applied for Feb. 1, 1887.^{528a, 528b, 528c, 528d, 528e, 529a, 529b, 529c, 529d, 529e, 530} It included the oxides of eleven other metals. Compounds of metals other than copper are claimed in subsequent patents, some of which ignore copper. The last appeared in 1900. It is of interest to note that the same inventor was responsible for the superheated-water process for mining sulfur.

It is claimed that 99.7% of the sulfur contained in an oil is

removed by passing its vapor through packed and compressed copper turnings.¹²¹³ Copper has been used for desulfurizing vegetable and animal oils.^{794a} The oxides of copper are desulfurizing agents.^{546, 798, 1170, 1236, 1263, 1291, 1484, 1646, 1673, 1725b} There are a host of articles and patents covering the use of copper, copper oxide or salts, either in liquid petroleum products or in their vapors.^{231, 330d, 331, 344, 354, 375, 528e, 603, 608c, 794b, 867, 890, 891b, 894, 945, 975, 976, 1099, 1127d, 1149a, 1162, 1170, 1205d, 1207, 1210, 1275a, 1276, 1277, 1355, 1481b, 1494, 1560, 1570b, 1645, 1647}

In some cases copper and its compounds appear to act catalytically in the oxidation of mercaptans to disulfides, while in others, the sulfur is removed as copper sulfide. Several kinds of reactions may be involved in what appears to be a simple operation.

The oxidation of glutathione by oxygen in the presence of copper ions depends on the *pH* of the solution, which should be above 7.¹⁷⁶⁰

Much attention has been given to the use of cupric chloride for the oxidation of mercaptans in the sweetening of petroleum distillates. It is used in a variety of ways, in solution or spread on the surface of a solid, such as bauxite. It may be considered as a catalyst or oxygen carrier for air oxidation. There are numerous articles on the use of copper chloride^{51, 314b, 717a, 729, 763, 846e, 864, 1054, 1414, 1443, 1626b} and many patents.^{102, 104c, 106, 110, 167, 226, 272, 332.5, 350b, 355b, 448c, 524, 525, 526, 703, 764b, 765a, 928b, 1089, 1090, 1127b, 1129b, 1138b, 1138c, 1255, 1262, 1328, 1435, 1439, 1444, 1445a, 1445b, 1657, 1662.}

The use of copper sulfate has been described¹⁶⁰¹ and several ways of applying it have been patented.^{355a, 448a, 1317, 1442a, 1462, 1516, 1660, 1681} Copper hydroxide,^{18b, 105, 862, 1020a, 1126c} various salts,^{302c, 328c, 544, 879, 1266a, 1733} acetate,^{608a, 608b} oil-soluble salts,²⁷⁹ naphthenates,^{646, 705, 764c} oleate,¹¹⁰⁸ and silicate^{1503b} have been recommended. Copper hydroxide may be mixed with the hydroxides of other metals.^{1205b} The use of an ammoniacal solution of a copper salt has been proposed.^{141, 318, 769, 1129b, 1159, 1774} Mercaptans may be converted to cuprous mercaptides which are removed by filtering through granular material,^{1129a, 1266b} or extracted by means of an alkyl amine.^{1531d} Means have been proposed for taking care of residual copper compounds remaining in the oil.^{104b, 380, 429, 1240c, 1417a, 1438a, 1442b, 1446, 1475, 1530c} Various units and cycles have been proposed.^{10b, 330b, 710, 1177, 1722}

Cadmium and Zinc

Cadmium mercaptides have been made as a matter of course, along with those of other heavy metals, by workers with mercaptans, but nothing of special interest has been recorded about them.^{881b} Pure *t*-butyl mercaptan has been prepared from the cadmium mercaptide.^{1001.5}

Cadmium nitrate has been used in analyses for the removal of hydrogen sulfide and mercaptans.¹¹⁷⁹ Cadmium hydroxide, in one way or another, has been suggested for the removal of mercaptans from petroleum products.^{40b, 150, 390c, 1205c, 1745d} Cadmium metal and salts have been recommended for the same purpose.^{333b, 612, 1503a}

The cadmium mercaptide from *o*-aminothiophenol is claimed as a fungicide and bactericide.¹⁵³⁴

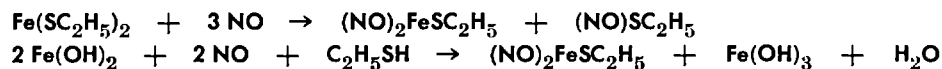
Zinc mercaptides are mentioned in many of the early articles on mercaptans but little is said about them. Zinc mercaptides are formed when disulfides are reduced by zinc.^{1226b, 1534} They dissolve readily in acid and thus are not isolated. They can be prepared from aryl mercaptans in an inert solvent and zinc oxide.¹⁰³¹ The mercaptides of zinc and of some other metals form persulfides which are said to be accelerators.⁹⁵

Silver

Silver mercaptides are readily formed and are extremely insoluble.^{387a, 739} This accounts for their use in qualitative tests for mercaptans and in their quantitative determination as outlined in the section on analysis. A coordinated silver mercaptide, $C_{10}H_{15}OSAg \cdot AgNO_3 \cdot H_2O$, is formed from thiolcamphor.⁴⁰³ Silver mercaptides which are soluble in thiosulfate may be added to a photographic fixing bath.⁵⁷³ Silver removes mercaptans from hydrocarbons.^{743a} Some silver mercaptides are said to have therapeutic value.¹¹⁵⁶

Iron, Nickel, and Cobalt

Dinitroso-iron mercaptide, $(NO)_2FeSC_2H_5$, m. 78° , is formed from ferrous mercaptide, or from mercaptan and ferrous hydroxide, and nitric oxide: ^{742, 1047a, 1329}



Ferrous hydroxide, mercaptan, and carbon monoxide give a complex, $\text{Fe}(\text{SEt})(\text{CO})_3$, m. 67° , which may have the double formula.¹³³⁰ The same compound is obtained from iron carbonyl and mercaptan. There is a similar one, $\text{Co}(\text{SEt})(\text{CO})_3$, from cobalt carbonyl.⁷²⁷ Iron carbonyl has been suggested as an agent for the removal of mercaptan.^{100a, 234d}

A complex nickel compound, $\text{Ni}_2(\text{NO})(\text{SEt})_3 \cdot 6\text{H}_2\text{O}$, is formed from a nickel salt, mercaptan, and nitric oxide. If nickel hydroxide is used instead of the salt, the product is $\text{Ni}(\text{NO})\text{SEt}$. Carbon monoxide decomposes this, forming nickel carbonyl.^{1047b, 1048, 1330} The poisoning of nickel catalysts by mercaptans has been studied.^{1357.5}

Nickel mercaptides, $\text{Ni}(\text{SR})_2$, are diamagnetic. Their properties indicate that they are high polymers. The nickel salt of dithiooxamide is also polymeric.⁸²⁶

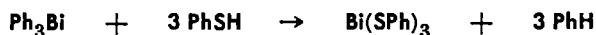
Antimony and Bismuth

These are mentioned here though they will be taken up in other chapters. The chief objective in making mercaptides of antimony and bismuth has been to get these elements into medicinals. The most of the compounds prepared have contained solubilizing groups, either salt forming or hydroxyl. These will be discussed in the chapters on mercaptoacids and on hydroxymercaptans.

The compounds of the general formula $\text{Sb}(\text{SR})_3$ may be regarded either as mercaptides of the metal antimony or as the esters of trithioantimonous acid. Actually they are liquids and behave more like esters. They will be mentioned in Chapter 3 along with esters of trithiophosphorous and trithioarsenious acids.

Since antimony chloride is hydrolyzed in water, except in the presence of an excess of acid, it is not convenient to make antimony mercaptides in the usual way. They can be obtained from anhydrous antimony chloride either with a sodium mercaptide or with a mixture of a mercaptan and a tertiary amine.⁹⁶² The higher members of the series have been prepared by adding the mercaptans, octyl to octadecyl, to a warm chloroform solution of antimony trichloride. Up to the decyl they are liquids, the higher are solids, dodecyl m. 40° , tetradecyl m. 51° , cetyl m. 52° and octadecyl m. 59° .^{1.5, 294, 295} The *p*-nitrophenyl mercaptide has been made similarly.¹⁷⁰¹

A few bismuth mercaptides have been made.⁶⁷³ The triethyl, $\text{Bi}(\text{SEt})_3$, a solid melting at 200° , appears to be a mercaptide rather than an ester which is in keeping with the metallic character of bismuth.^{881a, 962} The phenyl mercaptide, $\text{Bi}(\text{SPh})_3$, has been made by adding phenyl mercaptan to an acid solution of bismuth trichloride.^{909.5, 1624} It can be obtained from triphenylbismuth:



There are intermediate compounds, Ph_2BiSPh , m. 160° , and $\text{PhBi}(\text{SPh})_2$. A pentavalent compound, $\text{Ph}_3\text{Bi}(\text{SPh})_2$, m. 44° is known.⁵⁸⁰ Triethylbismuth reacts similarly.¹¹⁸²

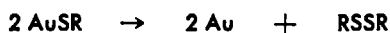
Antimony and bismuth compounds have been made from partially hydrolyzed keratin.¹⁷³⁵ Bismuth mercaptides have been proposed as therapeutic agents.^{408, 794c, 1156, 1515}

Gold, Platinum, and Palladium

Auric chloride and a mercaptan give an aurous mercaptide and the disulfide:



The mercaptide decomposes at 150° :⁷¹⁴



Some, at least, of the paints used in gilding china appear to contain gold mercaptides which decompose in this way during the firing. Gold mercaptides have been proposed as therapeutic agents.^{408, 794c, 797, 1156, 1515} Most of the compounds prepared for such use have contained solubilizing groups, either salt forming or hydroxyls. These will be taken up in chapters on mercaptoacids or on hydroxymercaptans.

Platinic mercaptide, $\text{Pt}(\text{SEt})_4$, decomposes in a vacuum at 100° into the platinous mercaptide and the disulfide.^{741a} Many complex compounds have been prepared starting with platinum or palladium mercaptides.^{278, 739, 1311c, 1311d, 1312}

Other Metals

Trimethylaluminum reacts to give dimethylaluminum methyl mercaptide, a liquid whose vapors give a molecular weight corresponding to $(\text{Me}_2\text{AlSMe})_2$.³³⁸

Tin mercaptides have been made, but there is little to say about them. Some have been claimed as mordants.⁸⁰² The stannic compounds, $\text{Sn}(\text{SR})_4$, are esters rather than mercaptides and are included in Chapter 3. The stannic phenyl mercaptide, $(\text{PhS})_4\text{Sn}$, is more reactive than the corresponding lead, mercury, and bismuth compounds.^{909.5} An alkali stannite has been recommended for taking out polysulfides.⁶⁶

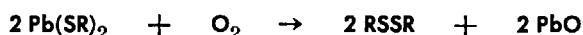
The compound, $(\text{MeS})_3\text{B}$, is trimethyl trithioborate and belongs in Chapter 3.^{231.5}

Several thallos mercaptides have been prepared.^{1, 881b}

Lead Mercaptides

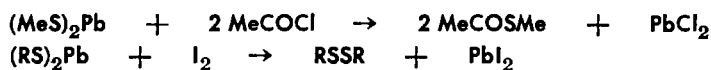
Lead mercaptides have been of great importance on account of their formation as intermediates in the well-known "doctor" process for sweetening gasoline.¹⁸² They are precipitated instantly when a mercaptan is added to an aqueous solution of a lead salt. For preparing the mercaptides from the mercaptans above dodecyl, the mercaptan is added to a boiling alcoholic solution of lead acetate. The mercaptides crystallize out on cooling.⁵¹⁴

The lead mercaptides are yellow and resemble organic compounds in being soluble in organic solvents and in having melting points.¹⁶⁹⁴ The lead mercaptides are oxidised by the oxygen of the air and become insoluble. There is little, if any, change in appearance. The products have peroxide properties.^{1225b} Some disulfide is formed also:¹¹⁴⁰



Triethyllead mercaptide, Et_3PbSEt , is from the reaction of triethyllead hydroxide with the mercaptan.⁶⁸⁶ Lead tetraphenyl and thiophenol give lead phenyl mercaptide, phenyl disulfide and benzene.^{909.5}

Lead mercaptides have been used for making other derivatives. They react much like the alkaline mercaptides: 182, 488, 514, 1211



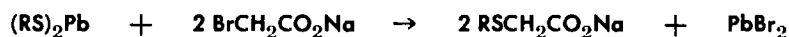
They are oxidised by nitric acid to the corresponding sulfonic acids.¹¹⁹⁴

At 180 to 190° a lead mercaptide decomposes into an alkyl or aryl sulfide and lead sulfide: 550, 881d, 1226c



As will be explained later, the mercaptans in a naphtha are changed to lead mercaptides by treatment with the "doctor" solution. These suffer 99% decomposition, according to the above equation, when the naphtha containing them is heated to 102° for 10 minutes or kept at 42° for 24 hours. This "sweetens" the gasoline and eliminates half of the sulfur.^{1057c} Converting the mercaptans into lead mercaptides by treatment with lead oxide ^{528a, 576a, 1020b, 1149a} or acetate ^{1389, 1625, 1663b} and distilling off the naphtha has been advocated as a method of sweetening.

It has been proposed to convert these lead mercaptides into water-soluble compounds by treating them with the sodium salt of a halogen acid: ⁴⁵⁶



Lead mercaptides, obtained from "sour" petroleum distillates, have been claimed as antiknock agents for gasoline.^{827b}

It has been proposed to sweeten oils by heating with lead ^{161, 256, 409, 604, 829, 832, 1117, 1493, 1685} or lead oxide.^{19b, 160, 576b, 824, 1127c, 1170}

Lead and manganese colophony salts and oleates are mentioned in an 1898 patent as desulfurizing agents.¹⁹⁹ Treatment with various lead compounds has been recommended for the desulfurization of vegetable oils.^{794b}

The "Doctor" Treatment

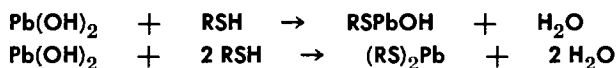
Reference must be made to reviews.^{531, 846c}

This treatment, long and extensively used for "sweetening" "sour" gasolines, involves two steps: the formation of lead mercaptides and the conversion of these into alkyl disulfides with the precipitation of lead sulfide.

Lead plumbite was used in 1895 by Mabery ^{1002a} for purifying kerosene, but no mention is made of any further treatment. It is mentioned in two patents to Henry ⁷⁰⁷ in 1898 and appears to have been followed by oxidation.

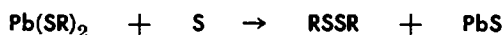
The "doctor" solution is prepared by dissolving litharge in aqueous sodium hydroxide which may be from 4 to 24%. The weaker solution dissolves about 1.5% of litharge and the stronger about 3%.^{446a} Doubtless sodium plumbite is the active constituent, but it is convenient to consider the alkali as only a mutual solvent for the mercaptans and the lead oxide.^{60, 1725b} When this solution is agitated with a sour naphtha, lead mercaptides are

formed. According to conditions, either one or two molecules of mercaptan may react with one of lead hydroxide:

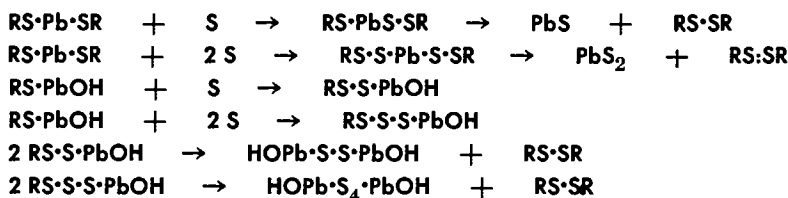


Both the basic and neutral lead mercaptides pass back into the hydrocarbon layer. Evaporation of this leaves the lead mercaptides as a yellowish mass, which is solid, pasty, or oily according to the mercaptans present.^{1225a}

The second step is the conversion of the lead mercaptides to the disulfides. This is effected by the addition of sulfur to the naphtha containing the mercaptides. The reaction is written:



This looks simple but is actually quite complicated. There are a number of reactions some of which appear to be: ^{411, 1225c}



The final result is that represented by the first simple equation; the mercaptan is oxidised to the disulfide which remains in the naphtha.

The amount of sulfur added should be just right. If too much is used, the gasoline is corrosive, if too little, lead mercaptides are left in it.^{1056a} The naphtha containing the lead mercaptides may be agitated with aqueous sodium polysulfide, which supplies the sulfur.^{1122b, 1595, 1596, 1597} Any excess sulfur may be taken out by agitating with sodium sulfide solution.¹⁴⁴ An oxidising agent precipitates the lead as oxide or hydroxide:



In the presence of alkali, this oxidation may be effected by air.^{309b} Various such agents have been recommended, hypochlorite,^{22b, 23, 174, 1010, 1190} hydrogen peroxide,^{187, 1240a} cupric chloride,⁶⁹⁵ or permanganate.⁹⁶ If lead plumbate is used in the first step, instead of a part or all of the plumbite, additional oxidising agent is not necessary.^{554, 863, 1500} The lead mercaptides are precipitated from solution by exposure to ultraviolet light.^{1126b}

The doctor solution may be used to take out elemental sulfur.^{781, 827a, 1483, 1687c}

The operation may be continuous^{636b, 654, 1527} and may be carried out at above 90°.^{828e} An alcoholic solution has been recommended.^{486b, 1687b} Certain organic compounds are claimed as solutizers.^{724a, 1141} Mercuric chloride,¹⁵⁸⁹ lead antimonate,⁸⁷⁸ and powdered antimony⁴⁰⁰ have been suggested as useful additions to the doctor solution.

The addition of hydrogen sulfide to the naphtha before treatment is said to be beneficial.^{1241, 1306}

There has been much discussion as to the role of lead sulfide in sweetening.^{1121b, 1686} It seems to serve as a catalyst in promoting the reactions involved.^{33, 1689} Experiments with several mercaptans added to sulfur-free naphtha showed that oxygen alone does not sweeten and the addition of lead sulfide does not help, but oxygen, lead sulfide, and sodium hydroxide do sweeten.¹¹⁴⁰ The lead sulfide acts as a catalyst when a sour gasoline is blown with air in the presence of sodium plumbite solution.⁹²⁵

The study of this effect lead to experiments in which lead plumbite, the characteristic constituent of the doctor solution was left out.^{1382, 1383, 1456} In the "Stratco" process, a naphtha is blown with sodium hydroxide in which lead sulfide is suspended.^{15, 40c, 1197, 1550, 1587b} Freshly precipitated lead sulfide is more effective.¹⁵⁵¹ A minor amount of cupric hydroxide is a useful addition to the sodium hydroxide and lead sulfide.^{1240b} Oxygen may be supplied by sodium peroxide.¹⁵⁸³ It is claimed that the sweetening process goes on in the absence of oxygen if the solution is kept substantially free of lead salts by the regulated addition of sodium sulfide.²¹⁷ After all, the lead plumbite may be present though it was supposed to have been left out. It is known that lead sulfide is oxidised easily to lead sulfate, which may dissolve in the alkali to form lead plumbite.

Sweetening is effected by treating an oil with alkali, lead sulfide, and sulfur.^{504, 783}

As far as odor is concerned the *doctor* treatment is entirely satisfactory.¹⁰⁴⁹ It is frequently combined with other treatments to give a finished product.^{12b, 436, 528c, 594, 953b, 1122a, 1283}

The regeneration of the doctor solution and the recovery of lead and other substances from it have received considerable attention but cannot be gone into here. A few references are given.^{10a.}

31, 35, 52, 120c, 321, 348, 373, 392, 414, 484, 500, 503b, 593b, 723a, 730, 751, 876, 1062, 1076, 1085, 1131, 1221a, 1243, 1299, 1307, 1315, 1413, 1407, 1543, 1621, 1656, 1715, 1716b

Various ways of using lead sulfide have been proposed.^{103, 539, 671b, 672a, 841b, 979, 999}

Lead naphthenate and sulfur, in the presence of water, are recommended for the removal of mercaptans.^{672b} An intimate mixture of calcium hydroxide, lead oxide, and sulfur has been proposed for sweetening naphthas.^{249a, 250} Gasoline may be treated with sodium hydroxide and sulfur and then with dry powdered lead plumbite.^{249b}

The doctor process is said to be applicable to the removal of mercaptans from secondary alcohols.⁴²

Many factors are involved in *doctor* sweetening.^{981, 983} A large volume would be required to describe its many modifications and its applications and adaptations to various oils. All that can be done here is to list a few articles^{141, 144, 197, 396, 430, 459, 561, 669b, 670, 706, 995, 1133b, 1486c, 1528, 1727, 1728, 1734} and some of the patents.^{97, 137, 146, 157, 207, 215, 234c, 237, 297, 330a, 336, 348, 441a, 460, 462, 503a, 509, 653, 659, 732, 746, 765b, 779b, 785, 836a, 841a, 858, 898, 915, 972, 982, 986, 1012, 1102, 1127a, 1205a, 1209, 1228, 1240d, 1357, 1457, 1467, 1474, 1511, 1531a, 1548, 1565, 1587a, 1655, 1687a, 1718}

Physical Methods for the Removal of Sulfur Compounds

These do not properly come under reactions of mercaptans but are mentioned briefly for the sake of completeness.

SOLVENT EXTRACTION

The refining of petroleum distillates would be beautifully simple if a solvent could be found which would selectively extract all of the undesirable and none of the desirable constituents. In spite of many efforts this dream has not been realized. Solvents have been found which dissolve the sulfur compounds preferentially but none that take them out completely and exclusively. A serious difficulty is that the good solvents for sulfur compounds are also good solvents for olefins, which are present in cracked distillates, and for aromatics, which abound in the catalytically cracked fractions. This is the same difficulty which has been encountered with sulfuric acid treatment. A few articles and patents are noted.

Liquid sulfur dioxide is the solvent most frequently recommended.^{12a, 12b, 69, 141, 202, 417a, 417c, 435, 436, 436.5, 454, 465, 630, 1138a, 1667b, 1734} It may be used with carbon dioxide,^{563, 1562} with propane,^{506, 1559} or with pyridine.⁵⁰⁷

Furfural has met with some favor.^{450, 624, 625, 1052, 1586a} Phenol, cresols and mixtures containing them,^{289a, 610, 1364, 1531c, 1552b} aniline,²⁷⁵ aminobiphenyl,^{289b} alcohols,^{233b, 530, 657, 676, 1615} aminoalcohols,^{1151, 1458} amines,¹⁷⁰⁸ glycols,^{1022, 1041c} formic esters,^{796a, 800, 997} nitrobenzene,^{501b, 1364} amyl acetate,¹⁵⁸⁴ acetone,^{21, 225, 1364, 1644} aldehydes,^{72, 383, 1731b} ethylene and propylene oxides,⁴³⁷ and water,⁹⁶⁷ particularly at a high temperature under pressure,^{46, 830} have been proposed. Phenol is recommended for lubricating oils.^{1552a}

At low temperatures, sulfuric acid may be considered as a selective solvent, but its use has already been discussed under oxidation. Phosphoric acid is of some value.^{121b}

Extractions with selective solvents are carried out extensively in the petroleum industry, but the removal of sulfur compounds is only incidental.^{845b}

DESULFURIZATION BY ADSORBENTS

While adsorption is primarily a physical process, it is frequently accompanied by oxidation, polymerization,^{192, 666, 667} and other chemical changes in the substance adsorbed. Probably all adsorbents are more or less selective, but none has been found that takes out sulfur compounds and nothing else. As was stated about selective solvents, olefins and aromatics tend to go along with the sulfur compounds. Adsorbents are used extensively in the petroleum industry for purifying oils, particularly for the less volatile types, but desulfurization is only one item. The elimination of gum formers and color bodies is usually the main objective. Oxidising³⁹³ and other agents are sometimes added. This subject can be treated only briefly here.

Silica gel is discussed in a number of articles.^{141, 188, 744, 754, 891a, 891b, 1056d, 1404c, 1665, 1667a, 1668, 1670a, 1670b, 1728, 1731a, 1761a} A chromatographic separation of paraffins, olefins, aromatics, and sulfur compounds can be made with a column of silica gel.^{385, 674} It is said to take thiophenol out of phenol.^{1417c} A few patents are listed.^{330c, 734, 752, 1417b, 1696} It may be combined with alumina gel^{1266c} which may be used alone.^{285, 1728} Alcohols and mercaptans may be separated by silica gel.^{48.5}

Fuller's earth,^{34, 240, 422, 581, 582, 608b, 629, 1728} clay,^{328a, 434, 890, 896, 1481a, 1663a} and bauxite^{38, 108, 200, 212, 367, 417a, 417c, 423, 425, 426, 628b, 723c, 762, 1340a} have received much attention. Activated charcoal^{286, 747, 796b, 891a, 1353, 1697, 1755, 1776} and other adsorbents^{3, 328b, 390c, 840a, 1049, 1050, 1080, 1098, 1556} have been recommended.

Various additions, methods of activating adsorbents by additions or by special treatments, and different ways of using them have been proposed but cannot be expanded on here.

DESULFURIZATION BY FREEZING

In some cases, a major portion of the hydrocarbons can be solidified by strong cooling and the sulfur compounds left in the liquid part.^{1199d} This method has been used to free benzene of thiophene.^{738, 1636}

SEGREGATION BY DISTILLATION

In some cases, considerable concentration of the sulfur in certain fractions, or in the residue, may be effected by careful fractionation, either straight or azeotropic. This may lighten the load on the desulfurizing process.^{645, 647, 932, 1103, 1391, 1445b, 1466b, 1530b, 1581, 1730}

Detection of Mercaptans

On account of the importance of mercaptans in the refining of petroleum products, much attention has been given to their detection and estimation. In practice, usually the "doctor" test is used for this purpose. A distillate supposed to contain mercaptans is shaken with lead plumbite solution from which it is separated. A hydrocarbon containing a small percentage of free sulfur is added. The formation of a black precipitate of lead sulfide indicates the presence of a mercaptan. If no such precipitate forms, the gasoline is said to be "sweet."^{1107, 1171, 1702} For the chemistry of this test, reference should be made to the section on the "doctor" treatment. It is extremely sensitive, capable of detecting a molar concentration of 0.00006% mercaptan.⁹²⁵ The sensitivity varies with the mercaptan, being 0.002% for methyl, 0.0002% for butyl, and 0.00009% for heptyl.¹⁹⁷ It has been maintained that it is unnecessary to refine a gasoline until it can pass so severe a test.^{381, 444, 669b, 670, 912, 984} It should be noted that diolefins and some terpenes react with the doctor solution.^{1121a, 1386} Organic peroxides give a dark

precipitate of lead peroxide in the doctor test.²⁰⁸ Standardized conditions for making the test are important.³⁶³

Conversely, the doctor test can be used to show the presence of sulfur in a naphtha. A mercaptan, such as butyl, is added to the suspected naphtha which is then shaken with the lead plumbite solution. Different authors give the sensitivity of this test as 2.5 to 20 parts of sulfur per million of gasoline.^{113, 983, 1057a, 1632, 1723}

There are several color tests for mercaptans. Isatin in sulfuric acid gives a green color with a mercaptan.^{368, 1339, 1613} A mixture of fuchsin, formaldehyde, and sulfuric acid will show the presence of mercaptans or of thioacids.¹⁵³⁵ Ferric chloride,^{881c, 1308} tetra-nitromethane, trinitrochloromethane, trinitrobromomethane,¹⁰⁰⁸ and chloropicrin¹³¹³ give colors. The alkyl thionitrates, RSNO, from nitrous acid, have distinctive colors, red for primary and secondary, and green for tertiary.¹³⁴⁸ Sodium nitroprusside is employed in several tests.^{661, 1056c, 1222, 1309, 1769} A red-violet color is produced by 0.0001% mercaptan sulfur in solvents or petroleum fractions. This is said to be the most sensitive test.^{533.5} It is quicker than the "doctor" test.^{826.5} Grote's reagent gives a purple-red color.⁶²⁷ The acceleration of the reaction of sodium triazotate with iodine can show the presence of a mercaptan.^{494, 495} This is more sensitive to mercaptans than to other sulfur compounds.^{56.5} Bismuthtriethyl and lead tetraethyl serve to detect the sulfhydryl group.^{578, 1182} A disulfide reagent, 2,2'-dihydroxy-6,6'-naphtholdisulfide, has been recommended as a reagent for detecting the presence of mercaptan groups in proteins.^{86.5} Mercaptans can be detected by the use of the blood of larvae of *actia caja*.¹⁴²¹

Gases containing mercaptan vapors may be passed through alcohol having mercuric oxide in suspension, or mercuric chloride¹³⁰ or cyanide^{127, 1185} in solution. An aqueous solution of cadmium chloride, or acetate, may be used.^{1021, 1171} By adjusting the acidity, a distinction can be made between mercaptans and hydrogen sulfide.^{1358, 1463} Liquid hydrocarbons containing mercaptans can be shaken with one of these solutions.¹⁵⁸⁵ Detailed directions of tests for aliphatic and aromatic mercaptans have been given.^{853.5}

The corrosion of a copper strip is a test much used industrially.^{49b, 407, 451, 669a, 1077, 1386} In making this test control of

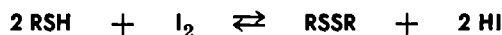
time and temperature is important.^{200, 1386} A silver strip is similarly affected.^{407, 1077} Mercury may also be used.^{1077, 1386} Elemental sulfur is even more corrosive than mercaptans³⁷ and must be eliminated before testing for mercaptans. The corrosive effects of several mercaptans have been compared with those of other sulfur compounds.⁸⁹⁷

Petroleum peroxides give a black precipitate with mercury.³⁹

Estimation of Mercaptans

Methods for determining mercaptans have been reviewed.^{292.5}

A commonly used method for determining mercaptans is the titration with iodine:



Since hydriodic acid is a strong reducing agent, the reaction does not go to completion unless it is removed. The mercaptan is dissolved in a hydrocarbon, such as benzene, under which there is a water layer to take care of the acid. A standard solution of iodine is run in as long as it is decolorized. Naturally, high values are obtained if unsaturates are present. This can be checked by titrating the acid in the water layer. By taking proper precautions, an accuracy of about 0.1% may be attained.^{870, 882, 1189a, 1217, 1378, 1385, 1405} An alcoholic iodine solution containing pyridine has been used.^{674.5} A tertiary mercaptan may take twice as much iodine and go to the sulfenyl iodide instead of the disulfide:^{899c}

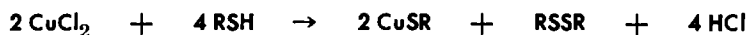


Much attention has been given to the iodometric titration of cysteine.^{922, 936, 989, 1482, 1634} The oxidation does not always stop at the disulfide stage, but may go on to cysteic acid.^{1472, 1473}

A mercaptan can be titrated with lead tetraacetate.⁹⁴⁶

It has been proposed to determine a mercaptan by its reducing action on cupric chloride. The resulting cuprous chloride is titrated with permanganate.¹⁴⁴⁰

When a mercaptan reacts with a cupric salt, a cuprous mercaptide is formed:



The cuprous mercaptide is a pale yellow and the disulfide is colorless, or nearly so. To determine a mercaptan, a standard

ammoniacal solution of a cupric salt is run in until the blue color persists.^{120a, 916, 1476} In order to have the reaction take place in a single phase, when a mercaptan is in hydrocarbon solution, a standard solution of cupric oleate or naphthenate in kerosene has been proposed. This is added as long as the color is changed to a pale yellow.¹⁷³ A cupric alkyl phthalate may be substituted for the oleate. Cupric octyl phthalate, which is readily soluble in hydrocarbons, is used for mercaptans in gasoline, while cupric butyl phthalate is suitable for alcoholic solutions.¹⁶⁰⁹ The cupric oleate method has been used for determining mercaptan warning agents in natural gas.^{577, 1233, 1499} Cupric acetate has also been used for this purpose.^{456.5}

✓ Silver nitrate is particularly useful in the detection and estimation of mercaptans. A black precipitate with it is a sensitive test for the presence of mercaptans in distillates.¹¹⁷¹ This has been compared with the *doctor* test.¹¹⁰⁷ As the precipitation of silver mercaptides is quantitative, this gives a method of estimation. A naphtha, from which hydrogen sulfide has been removed, is shaken with a measured volume of standard silver nitrate solution, the excess of which is determined by titration.¹⁸⁴ The original method has been modified and improved in various ways.^{25, 78, 101, 1043, 1045b, 1056b, 1606b, 1723} The silver mercaptides may be filtered off and weighed.⁹³¹ Elementary sulfur does not interfere.¹⁴¹⁸ An automatic recorder for plant control uses silver nitrate.¹²⁸²

Mercaptans can be titrated potentiometrically^{340, 1572, 1573} or amperometrically^{521, 899b, 900, 1373, 1545} with the aid of silver nitrate. An acidimetric method is based on the liberation of acid by the reaction of a mercaptan with silver sulfate^{1056b} or mercuric chloride.¹⁴⁰⁵ A polarographic method has been proposed.^{570.5}

A mercaptan can be determined colorimetrically by the aid of phosphotungstic acid.^{1430b}

A single volatile mercaptan, resulting from a chemical reaction, may be distilled into a lead acetate^{1185, 1189b, 1385, 1459} or mercuric cyanide solution.^{127, 1185, 1457.5} By weighing the precipitate and determining its metal content the amount and molecular weight of the mercaptan can be found.

The widely used lamp method for the determination of the total sulfur in distillates^{49a, 823, 1057b, 1447} is applicable to mercaptans,^{583, 1762} but only when no other sulfur compounds are

present. It may give low results with mercaptans, particularly when large amounts are present.^{476, 1670b, 1670c} Since a large sample of the naphtha may be burned, the lamp method is particularly applicable to the estimation of small percentages of sulfur compounds. An aryl mercaptan can be oxidised over platinum gauze at 900° and the sulfur weighed as barium sulfate.^{495.5}

The opposite of the lamp method is passing the hydrocarbon, containing the sulfur compounds, with hydrogen, over a catalyst which converts them to hydrogen sulfide, which is determined.^{1392b}

In the determination of a mercaptan in the oxygen bomb, the oxygen pressure should not be less than 35 atmospheres.^{387b} Lead nitrate may be used to precipitate the sulfuric acid.^{1731c} There is always the possibility of the formation of more or less of a sulfonic acid which resists further oxidation and is not precipitated by barium or lead ions.⁶¹⁶ The bomb method is not applicable to low percentages of sulfur compounds, since the size of the sample is limited. The Parr bomb may be used.^{445a} It is subject to the same limitations as to size of sample. Preliminary oxidation of the mercaptans with bromine or nitric acid reduces their volatility.^{1671a}

A given petroleum distillate may contain hydrogen sulfide, free sulfur, alkyl sulfides and disulfides, and thiophenes, along with mercaptans. The usual question is: How much of the total sulfur is accounted for by each of these classes? To answer this requires a number of analyses and some arithmetic. Several schemes have been proposed.^{101, 213, 486a, 551, 846b, 1237, 1689} The total sulfur is determined, usually by the lamp method. Hydrogen sulfide is removed by shaking with cadmium chloride or sodium bicarbonate²¹³ solution, and free sulfur with mercury. Mercaptans are determined by any appropriate method. Disulfides are reduced by zinc and acid and estimated as mercaptans. Some determinations may be made in succession and some on aliquots. Alkyl sulfides are precipitated with mercurous nitrate or titrated with bromine.¹⁰¹ Any undetermined sulfur is credited to thiophenes.

To determine mercaptans in a sodium hydroxide solution which has been used to extract them, the solution is acidified and extracted with a sulfur-free naphtha. They are then estimated in the hydrocarbon.⁹⁰⁶

Conversely, mercaptans can be used as analytical reagents.

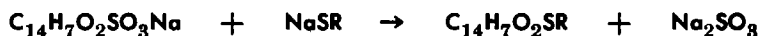
One in particular, 3,4-toluenedithiol, serves well for the detection and estimation of molybdenum, tungsten, rhenium, and tin, with which it gives distinctive colors.^{74, 134, 280, 658, 1096, 1274, 1478} 2-Mercaptobenzoxazole serves for the determination of rhodium.¹³⁹⁴ Several substituted mercaptoimidazoles give characteristic colors with heavy metals.⁹²³ The extensive use of 2-mercaptobenzothiazole for this purpose will be discussed when this compound is considered in a later chapter.

Ethyl mercaptan has been employed in the separation of the metals of the platinum group. It gives a yellow coloration with a solution of 1 part of palladium in 1 million parts of water.¹¹⁶⁹

Identification of Mercaptans

The mercuric derivatives, $(RS)_2Hg$, which were among the first mercaptides to be prepared, have convenient melting points and have been used frequently for identification.^{139a, 267, 1264} They serve well for distinguishing the isomeric propyl and butyl mercaptans. Their melting points are given in Table 11.2, along with those of other derivatives. *s*-Butyl mercaptan has been identified by the mercury derivative *s*-BuSHgCl.⁵²² The lead mercaptides have been prepared, but their melting points are not satisfactory and get worse on recrystallization.⁵¹⁴ This is probably due to air oxidation.^{1225b}

The alkyl α -anthraquinone sulfides are easily prepared from the mercaptans in alkaline solution with a salt of α -anthraquinone sulfonic acid:



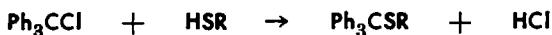
With the higher mercaptans, some alcohol should be added to promote solution. These sulfides crystallize well and have good melting points. They can be oxidised to the sulfones.^{458a, 737, 1326}

The *p*-nitrophenyl alkyl sulfides, $NO_2C_6H_4SR$, melt low but can be oxidised to sulfones.¹⁶⁵⁴ The 2,4-dinitrophenyl alkyl sulfides, $2,4-(NO_2)_2C_6H_3SR$, which can be made from 2,4-dinitrochlorobenzene and the mercaptide, and their sulfones are good derivatives.^{189, 190}

The melting points of the aryl *p*-nitrothiobenzoates, $p-NO_2C_6H_4COSAr$, are conveniently high, but those of the alkyl esters are too low.⁶²² The alkyl 3,5-dinitrothiobenzoates melt somewhat higher but hardly high enough. The 3-nitrothio-

phthalates melt high enough, but the spread is small.¹⁶⁹⁴ Pseudo-saccharin chloride gives satisfactory derivatives with many aliphatic mercaptans.^{1074.5}

Triphenylmethyl chloride reacts with a mercaptan in ether solution:



The methyl derivative melts at 105°, the ethyl at 125°, and the phenyl at 105°. ¹⁰⁹³ This looks like a promising reagent. Diphenylcarbonyl chloride, Ph_2NCOCl , reacts with mercaptans to give Ph_2NCOSR . The ethyl ester melts at 108° and the benzyl at 125°. ⁴⁸¹ More of these should be made.

The melting points of a number of these derivatives are given in Table 11.2. An inspection of the data shows that much remains to be done. There are many blanks in the table, particularly with the higher mercaptans and several of the series show rather narrow spreads.

The mercury derivatives serve for some of the mercaptans. For the normal mercaptans, the spread is not great and data are lacking for the higher. The α -anthraquinone derivatives for the lower mercaptans are good but are also lacking for the higher. The *p*-nitrophenyl sulfones are good as far as they go but their preparation involves two steps. The only series that are fairly complete are IV and V, 2,4-dinitrophenyl sulfides and sulfones. As the sulfones are made from the sulfides by a simple oxidation, two derivatives are made from one sample of mercaptan. Except for the first three members, the spread is not large in either series. The melting points of the 3,5-dinitrobenzoates, series VI, are inconveniently low. So far as made, all of the 3-nitrophthalates melt between 132° and 149°.

Physiological Effects

Methyl mercaptan acts on the central nervous system of fish to produce paralysis.²⁹⁹ It is relatively nontoxic, 0.5% by volume of the vapor being required to produce paralysis in rats.⁹⁶⁵ The toxicity of ethyl mercaptan vapors has been compared with that of other vapors.¹⁰¹³ It depresses the activity of catalase and peroxidase ^{317, 1101} and inhibits the growth of yeast,⁵⁸⁹ but may serve as a source of sulfur for the growth of cellar mold.⁸⁶⁸ It counteracts chloropicrin.⁷⁰ Less than 1% in anesthetic ether has little

TABLE 11.2

Melting Points of Some Mercaptan Derivatives

	I *	II *	III *	IV *	V *	VI *	VII *
Methyl	176 ^{a,1}	221 ^b	142.5 ^k	128 ^{1,3}	189.5 ^l	—	—
Ethyl	85 ^b	184 ^b	138.5 ^k	115 ^{1,4}	160 ^l	62 ^c	149 ^c
Propyl	72 ^c	151 ^b	114 ^k	84 ^{1,5}	127.5 ^l	52 ^c	137 ^c
Butyl	86 ^{c,2}	112.5 ^b	56.4 ^k	66 ^l	92 ^l	49 ^c	144 ^c
Amyl	75 ^c	128.8 ^l	—	80 ^l	83 ^l	40 ^c	132 ^c
Hexyl	58 ^d	113.9 ^l	—	74 ^l	97 ^l	—	—
Heptyl	77 ^c	95.9 ^l	—	82 ^l	101 ^l	53 ^c	132 ^c
Octyl	71 ^d	95.2 ^l	—	78 ^l	98 ^l	—	—
Nonyl	—	117 ^l	—	86 ^l	92 ^l	—	—
Decyl	—	—	—	85 ^m	93 ^m	—	—
Undecyl	—	—	—	90 ^m	97 ^m	—	—
Dodecyl	—	—	—	89 ^m	101 ^m	—	—
Tridecyl	—	—	—	94.5 ⁿ	101.5 ⁿ	—	—
Myristyl	—	—	—	94 ⁿ	104.5 ^p	—	—
Pentadecyl	—	—	—	—	—	—	—
Cetyl	—	—	—	96 ^{n,6}	105 ^m	—	—
Heptadecyl	—	—	—	99 ⁿ	106.5 ⁿ	—	—
Octadecyl	—	—	—	97.5 ⁿ	107.5 ⁿ	—	—
<i>i</i> -Propyl	63 ^c	134 ^j	115.3 ^k	94 ^{c,7}	—	84 ^c	145 ^o
<i>i</i> -Butyl	95 ^c	144 ^j	73 ^k	76 ^{p,8}	105 ^p	64 ^c	136 ^o
<i>s</i> -Butyl	189 ^e	—	—	—	—	—	—
<i>t</i> -Butyl	160 ^f	—	—	—	—	—	—
<i>i</i> -Amyl	100 ^c	86 ^j	—	80 ^p	—	43 ^c	145 ^c
<i>t</i> -Amyl	60 ^g	—	—	—	—	—	—
Cyclohexyl	78 ^o	—	—	148 ^{m,9}	172 ^m	—	—

* I = (RS)₂Hg, II = α -Anthraquinone SR, III = *p*-O₂NC₆H₄SO₂R, IV = 2,4-(O₂N)₂C₆H₃SR, V = 2,4-(O₂N)₂C₆H₃SO₂R, VI = 3,5-(O₂N)₂C₆H₃COSR, VII = 3-Nitrophthalic.

References

^a 153	^o 1347	^l 458a	^m 189	^q 242.5
^b 1764d	^f 1349	^j 737	ⁿ 514	^r 1703.5
^c 1694	^g 816	^k 1654	^o 1677	^s 1761.5
^d 1053	^h 1326	ⁱ 190	^p 188.5	^t 1517.5

Other data

¹ 178°, ¹⁵²	² 85°, ¹⁵³ , ¹⁰⁶⁸	³ 126°, ^{1708.5}	⁴ 113°, ^{1708.5}	⁵ 81°, 83.5°, ^{242.5}	⁶ 95°, ^{188.5}
⁷ 92°, ^{242.5}	⁸ 72°, ^{1708.5}	⁹ 147°, ^{242.5}	^{145°} , ^{1761.5}	^{146°} , ^{1517.5}	

effect.¹⁹⁶ A review has been written on the toxicology of aliphatic mercaptans.^{25,5} *m*-Nitrothiophenol has been compared with a number of other compounds as an anticoccidial agent.^{1654,5} The

thiocresols are about four times as toxic as the cresols.⁵⁷¹ Thiophenol lowers the blood sugar in rabbits.^{1389.5}

The relations between the structure of thiols and their reactions with antibiotics have been traced.²⁶⁴ Streptomycin is inactivated by β -aminoethyl mercaptan and by cysteine.³⁷⁰ The activation of papain by various mercaptans has been studied.¹⁴⁵¹

Ethyl mercaptan breaks the dormancy of potato tubers^{1100, 1101} and *p*-thiocresol does the same for peach buds.⁶³⁵

It was noted that the parts of roots in which growth by cell division normally occurs most rapidly gave the strongest test with nitroprusside, indicating a concentration of sulfhydryl compounds.³⁶ Ethyl mercaptan improves the root system of tobacco.¹²¹⁸ These observations led to experiments on the skin of animals and eventually on humans. These have demonstrated that mercaptans do aid in the healing of wounds. The one used most extensively has been *p*-thiocresol with benzyl mercaptan in second place.^{70, 505, 660, 662, 664, 665, 1118, 1331, 1332, 1333, 1335, 1336, 1600, 1712} It has been found that thioglucose^{663, 1334} and thioglycerol^{1566, 1567} are also effective.

Uses of Mercaptans

AS INTERMEDIATES

The industrial uses of mercaptans are small compared to those of some other classes of organic compounds, such as alcohols and amines, but some of them are important. The disagreeable odors of the lower mercaptans have been a serious handicap. Only recently have the higher mercaptans become available.

The reactivity of mercaptans and the variety of compounds that can be made from them make them attractive starting materials. Ethyl mercaptan has long been employed as one of the starting materials for making sulfonal, $\text{Me}_2\text{C}(\text{SO}_2\text{Et})_2$. The lower mercaptans, which are obtained in the process of refining gasoline, are available in quantity and await applications.

Methyl mercaptan has come into demand for the industrial synthesis of methionine.

Mercaptans may be starting materials for making plastics,^{958, 1419, 1533} wetting agents, pharmaceuticals and insecticides.^{1422b}

Mercaptans can be made to combine with acetylene to give vinyl sulfides, $\text{RSCH}:\text{CH}_2$, to which mercaptans can be added,

giving derivatives of ethanedithiol, $\text{RSCH}_2\text{CH}_2\text{SR}'$. These products have various uses.^{806a}

AS ODORS

The powerful odor of ethyl mercaptan, which has been against other uses, makes it desirable for disclosing leaks in distribution systems for natural gas. About eight pounds per million cubic feet of gas is sufficient to disclose leaks in underground pipes.^{1161, 1408} It may be added to methyl chloride and other refrigerants as a warning agent.³⁸⁹ Amyl mercaptan also has been recommended for this purpose.¹⁵⁹³ Butyl mercaptan has been used for emergency warning in mines.⁶⁷⁷ "Cal-Odorant," presumably a mixture of the lower mercaptans from the refining of high-sulfur petroleum, is used as an odorant in natural gas.^{356, 758, 1392a}

During World War I, *n*-butyl mercaptan was proposed as a camouflage gas. A quantity of it was manufactured at the American University in Washington, but there is no record of its use.²⁷

AS ANTIOXIDANTS AND INHIBITORS

The antioxidant and stabilizing power of mercaptans is attributed to the removal of catalytic quinones.⁸²¹ Mercaptans in general, and thioglycolic acid in particular, inhibit the catalytic effect of copper salts in oxidation.^{1430a}

Various mercaptans are claimed as stabilizers for polysulfone resins.⁸¹⁸ Butyl mercaptan, 0.1% or less, stabilizes chlorine compounds, such as carbon tetrachloride, trichloroethylene and perchlorethylene.^{397, 1540} Ethyl mercaptan stabilizes ethylene sulfide and similar cyclic sulfides.^{1199a} *n*-Hexyl and β -naphthyl mercaptans are recommended as antioxidants for white oil, a petroleum product.¹⁴⁹¹ Lauryl mercaptan and 2-mercaptobenzothiazole are claimed as stabilizers for pyrethrum-DDT aerosol mixtures.¹⁷⁵⁷ *t*-Butyl and other mercaptans stabilize alkyl thionitrites in fuel blends.³²⁴

In the pickling of steel sheets, 0.03% of *i*-propyl, *i*-amyl, benzyl or β -naphthyl mercaptans is said to be sufficient as an inhibitor.²⁴³ The higher alcohols, which are by-products in the methanol synthesis, may be turned into mercaptans for this use.⁹⁶⁶ The decomposition of tetralin peroxide is greatly influenced by the presence of propyl and phenyl mercaptans.¹⁷⁵⁴

Unsaturated fatty oils are said to be stabilized by reacting with

a higher mercaptan in the presence of a catalyst.¹⁶⁶⁴ Molding powders are improved by the addition of a small amount of a mercaptan.^{533, 1079}

One per cent, or less, of a mercaptan and an aliphatic amine prevent gum formation in cracked petroleum distillates.^{234b} A selenomercaptan has the same effect.^{1377, 1540.5} Mercaptans are useful in various oils.³⁶⁰ They prevent corrosion by antifreeze liquids.^{290, 428b} Certain mercaptans are added to lubricating oils to prevent bearing corrosion.^{433, 1632.6} β -Alkylaminomercaptans, $\text{RNHCHMeCH}_2\text{SH}$, in which R may be lauryl or cyclohexyl, are recommended as oxidation retarders.^{795c} A colloidal dispersion of zinc salts and mercaptans added to latex improves its qualities.²⁶⁶ A study has been made of the addition of mercaptans to petroleum products.^{257.5}

The use of mercaptans to control polymerization is probably connected with their antioxidant properties. They may be used to modify the polymerization of various monomers,^{312.5, 428c, 898.5, 1658} of butadiene,^{795b} of other hydrocarbons,³⁰⁵ and of methyl methacrylate.^{108, 298} They lead to synthetic rubbers of improved qualities.^{545, 1064} Studies have been made of the relation of the thiol structure to this effect⁵²¹ and of the reaction of the thiol with the catalyst.²⁴⁸ The role of mercaptans in regulating polymerization has been discussed.^{864.5} This use of mercaptans has grown to large proportions.^{92, 613, 795b, 899a, 913, 1143, 1504}

Mercaptans promote the isomerization of straight-chain paraffins to branched⁴⁹³ and of α,β -unsaturated acids from the *cis* to the *trans* form.¹⁴⁵³

AS PESTICIDES

Mercaptans and mixtures containing them have been tried out as pesticides.^{128, 223, 372, 637, 795a, 917, 966, 1341, 1599.5, 1638, 1756} Mercaptans and other sulfur compounds prepared from chlorinated higher aliphatic hydrocarbons are said to be useful in combating pests.⁷⁹⁹ Lauryl mercaptan is claimed as an insecticide and fungicide.⁶⁰⁰

Ethyl mercaptan has been tried against a number of insects with varying success.^{1114, 1178, 1522} Of five lower mercaptans, it is the most toxic to rice weevils, 17 mg. per liter.¹³⁶⁰ It increases the attractiveness of food to flies.^{924, 1234} Butyl mercaptan was found to be a repellent for white rats, but not for ordinary wild rats.⁵¹³

It repels flies^{924, 1234} and is a fumigant against weevils.^{1178, 1360} Phenyl mercaptan increases the effectiveness of hydrocyanic acid somewhat.¹²⁸⁸ β -Thionaphthol is moderately effective against mosquito larvae²⁴⁵ and aphids,¹³⁵⁰ but not against Japanese beetles.⁵¹⁰ It is not toxic to silk worms,⁵⁸⁵ but damages bean foliage.¹¹¹⁵

IN FLOTATION

Mercaptans are useful in flotation along with the widely used xanthates. Terpene mercaptans are recommended.^{177, 1310, 1390} Mercaptans alone, or mixed with alkyl sulfides, are claimed for the flotation of copper sulfide ores.^{720, 988, 1148} Sodium, zinc and lead mercaptides are said to be useful in flotation.^{860, 1105} The mixed mercaptans from the higher alcohols of the methanol synthesis are claimed.⁹⁶⁶

MISCELLANEOUS USES

Thiocresol aids the dispersing of Paris green in water.¹¹⁶⁰ A linear polymer can be made by the reaction of a diisocyanate with a dithiol such as decamethylene dimercaptan.²⁶¹ Resins can be obtained by heating phenol and sulfur chloride with a mixture of mercaptans, such as is extracted from petroleum.^{1454b} Mercaptoethylamines, $\text{HSCH}_2\text{CH}_2\text{NHR}$ and $\text{HSCH}_2\text{CH}_2\text{NR}_2$, may be starting materials for making vulcanization accelerators.^{808b} 2-Mercaptoarylthiazoles serve the same purpose.⁸⁰³ Sulfurized turpentine or pine oil, supposed to contain terpene mercaptans, is recommended as a plasticizer for chlorinated rubber.¹²²⁴

Polymeric organic sulfides are plasticized by the joint action of a mercaptan and an unpolymerizable disulfide.⁸¹¹ The addition of multivalent metal salts of a terpenethiol reduces materially the milling time in compounding rubber.¹⁶³³ Particular concentrations of ethyl mercaptan stabilize colloidal solutions of sulfur.⁸¹⁹ In alkaline solution, mercaptans have a depilatory action which may be utilized for removing hair from hides.^{1610, 1611, 1719} They may be constituents of depilatories for human use.^{480, 1388} The use of mercaptans in hair waving will be taken up in connection with thioglycolic acid. The addition of a small amount of a mercaptan to a fuel is said to suppress carbonization of metal parts.^{1632.4} In the oxidation of methanol to formaldehyde, mercaptans are claimed to diminish the formation of undesirable by-

products.^{1243,5} It is reported that thiophenol, used in the high-temperature digestion of wood, gave marked improvement in plastic properties.^{654,5} Mercaptans are used in one way or another in making extreme-pressure lubricants.^{337, 483, 1293, 1294} Ethyl and butyl mercaptans are said to aid in the production of asphalt from petroleum residues.¹⁰¹⁴ Octadecyl mercaptan and sulfide have been recommended for the moistureproofing of Cellophane.²⁷⁷

BIBLIOGRAPHY

1. R. K. Abbott, Jr., Iowa State Coll. J. Sci., 18, 3-5 (1943)—C.A. 38, 62.
- 1.5. Abbott Laboratories, Brit. pat. 669,304 (1952)—C.A. 46, 7113.
2. Victor Abeles, U.S. pat. 2,378,382 (1945)—C.A. 39, 4470.
3. G. W. Acheson, U.S. pat. 1,570,193 (1926); Can. pat. 264,216 (1926)—C.A. 20, 817, 3805.
4. C. E. Adams and T. B. Tom to S. O. Co. of Ind., (a) U.S. pat. 2,413,938 (1947); (b) 2,425,776 (1947); (c) 2,425,777 (1947); (d) 2,427,083 (1947)—C.A. 41, 1420, 7739.
5. Alexander Adiassewich, Ger. pat. 159,262 (1905)—C. 1905, I, 1062.
6. E. Adirovich, Aeta Physicochim. USSR, 21, 283-8 (1946)—C.A. 40, 7580.
7. P. H. W. Agren to A. Johnson & Co., U.S. pat. 2,422,875 (1947)—C.A. 41, 7100.
8. A. G. F. Theer & Erdöl Ind., Ger. pat. 130,679—J. Chem. Soc., 82, I, 714 (1902).
9. Jan Al and F. R. Moser to N. V. Bataafsche, U.S. pat. 1,819,055 (1931); Ger. pat. 535,848 (1929)—C.A. 25, 5733; 26, 1046.
10. J. C. Albright, (a) Natl. Petroleum News, 28, No. 38, 24H (1936); (b) *ibid.*, 29, R-211-12, 214, 216 (1937); Petroleum Refiner, 18, 91-5 (1939); (c) *ibid.*, 17, 437-40 (1938); (d) Petroleum Engr., 12, No. 8, 79-80 (1941)—C.A. 32, 757; 33, 7999, 354; 35, 6098.
11. J. G. Allen to Phillips Petroleum Co., U.S. pat. 2,414,626 (1947)—C.A. 41, 2886.
12. Allgemeine Ges. chem. Ind., (a) Ger. pat. 333,168 (1917), 372,724 (1923); (b) 469,289 (1927); Fr. pat. 641,312 (1928)—C. 1923, IV, 36; C.A. 23, 1259; C. 1929, I, 336.
13. J. C. Alspaugh to S. O. Dev. Co., U.S. pat. 2,397,077 (1946)—C.A. 40, 3890.

14. J. A. Altschuler, *Oil Gas J.*, **42**, No. 49, 137, 141 (1944)—C.A. **39**, 3417.
15. J. A. Altschuler and F. G. Graves, *Proc. Am. Petroleum Inst.*, 7th Mid-Year Meeting, Sect. III, **18**, 17–22 (1937); *Refiner Natural Gasoline Mfr.*, **16**, 272–6 (1937)—C.A. **31**, 8168.
16. J. A. Altschuler, F. G. Graves, and E. S. Brown, *Natl. Petr. News*, **29**, 12, 71–6 (1937); *Oil Gas J.*, **35**, No. 45, 129–30, 133, 135–6, 138, 140 (1937); *Refiner Natural Gasoline Mfr.*, **16**, 181–7 (1937)—C.A. **31**, 5551, 8903.
17. H. A. Alves and B. L. MacKusick to Pure Oil Co., U.S. pat. 2,394,652 (1946)—C.A. **40**, 2610.
18. O. P. Amend, (a) Can. pat. 61,892 (1898); U.S. pat. 601,331 (1898); (b) 747,347, 747,348 (1903); 764,099 (1904).
19. O. P. Amend and J. H. Macy, (a) U.S. pat. 480,311, 480,312 (1892); (b) 551,941 (1895).
20. R. C. Amero and W. H. Wood, *Oil Gas J.*, **46**, No. 3, 82–5, 99 (1947)—C.A. **41**, 4913.
21. E. André, *J. pharm. chim.*, **25**, 156–9 (1937)—C.A. **31**, 7238.
22. Anglo-Iranian Oil Co., (a) Ger. pat. 419,225; (b) Fr. pat. 725,186, 725,187 (1931)—C.A. **26**, 4943.
23. Anglo-Iranian Oil Co., and A. E. Dunstan, *Brit. pat.* 364,204 (1930)—C.A. **27**, 1744.
- 23.5. Anglo-Iranian Oil Co., F. A. Fidler, R. A. Dean, and T. V. Cullum, *Brit. pat.* 681,711 (1952)—C.A. **48**, 2759.
24. Anglo-Iranian Oil Co. and L. C. Strang, *Brit. pat.* 602,097 (1948)—C.A. **42**, 7976.
25. Anon., *Am. Gas J.*, **162**, No. 6, 47, 60 (1945)—C.A. **39**, 3413.
- 25.5. Anon., *API Toxicol. Rev.*, Sept. 1948, 3 p.—C.A. **43**, 5513.
26. Anon., *Iron Coal Trades Rev.*, **117**, 719 (1927).
27. Anon., *Moniteur scient.*, [5] **9**, II, 149–58 (1919)—C. **1919**, III, 1074.
28. Anon., *Natl. Petroleum News*, **32**, No. 14, R 115–6 (1940).
29. Anon., *Petr.*, **26**, 782–4 (1930).
30. Anon., *Petr. Times*, **24**, 259 (1930).
31. Anon., *Refiner Natural Gasoline Mfr.*, **4**, No. 12, 23–4 (1925).
32. Anon., *Refiner Natural Gasoline Mfr.*, **17**, 434–6 (1938).
33. Anon., *Refiner Natural Gasoline Mfr.*, **18**, No. 9, 96 (1939).

34. Anon., Refiner Natural Gasoline Mfr., 19, No. 4, 73-6, 77-80 (1940).
35. Anon., Refiner Natural Gasoline Mfr., 19, No. 4, 83-4 (1940).
36. Anon., Syn. Org. Chem., 3, 5 (June) (1930)—J. Chem. Ed., 7, 12, 2991 (1930).
37. Anon., U.S. Bur. Mines, Tech. Paper, 323 B.
38. Anon., U.S. Geol. Survey Bull. 365.
39. A. von Antropoff, J. prakt. Chem., [2] 77, 273 (1908)—C.A. 2, 2185.
40. F. A. Apgar to Sinclair Refg. Co., (a) U.S. pat. 1,735,988 (1929); (b) 2,365,993 (1944); (c) 2,367,178 (1945)—C.A. 24, 718; 39, 4470, 2868.
41. F. A. Apgar and C. A. Day, Jr., Oil Gas J., 38, No. 46, 187, 188, 243 (1940)—C.A. 35, 3070.
42. F. M. Archibald and C. M. Beamer to Standard Alcohol Co., U.S. pat. 1,995,597 (1935)—C.A. 29, 2973.
43. F. M. Archibald and Philip Janssen to Standard Alcohol Co., U.S. pat. 2,035,449 (1936)—C.A. 30, 3630.
44. E. G. Ardagh, W. H. Bowman, and A. S. Weatherburn, J. Soc. Chem. Ind., Trans., 59, No. 2, 27-40 (1940)—C.A. 34, 3733.
45. James Armstrong, U.S. pat. 837,655 (1906)—C.A. 1, 650.
46. G. B. Arnold and H. V. Atwell to The Texas Co., U.S. pat. 2,402,799 (1946)—C.A. 40, 6252.
47. R. C. Arnold, A. P. Lien, and R. M. Alm, J. Am. Chem. Soc., 72, 731-3 (1950)—C.A. 45, 2852.
48. G. W. Ashworth to Monsanto Chem. Co., U.S. pat. 2,268,467 (1941)—C.A. 36, 2567.
- 48.5. R. J. Askavold to Pure Oil Co., U.S. pat. 2,647,150 (1953)—C.A. 48, 7622.
49. ASTM Standard Method of Test, (a) D90-47T; (b) D130-30.
50. L. C. Atchison, Petr. Eng., 1, No. 10, 164 (1930).
51. R. G. Atkinson, Natl. Petroleum News, 32, No. 50, R-450-4 (1940)—C.A. 35, 1611.
52. Atlantic Refining Co., Chem. Met. Eng., 38, 76-7 (1931).
53. W. C. Ault and C. A. Hochwalt to Monsanto Chem. Co., (a) U.S. pat. 2,105,464 (1938); (b) 2,192,174 (1940)—C.A. 32, 2338; 34, 4897.
54. W. Autenrieth, Ann., 259, 363-4 (1890).
55. W. Autenrieth and Alfred Geyer, Ber., 41, 4256-8 (1908)—C.A. 3, 647.

56. W. Autenrieth and K. Wolff, Ber., 32, 1370-5 (1899).
- 56.5. W. Awe and E. Naujoks, Oesterr. Apoth.-Ztg., 6, 534-6 (1952)—C.A. 47, 6608.
57. W. N. Axe to Phillips Petroleum Co., U.S. pat. 2,416,465 (1947)—C.A. 41, 3955.
58. F. C. Axtell to Axtell Research Labs. Inc., (a) U.S. pat. 1,677,425 (1928); (b) 1,645,679 (1927); Brit. pat. 282,738 (1926)—C.A. 22, 3289, 162, 3984.
59. Axtell Research Laboratories, Inc., Fr. pat. 646,134 (1927)—C.A. 23, 2290.
60. G. W. Ayers, Jr., Oil Gas J., 28, No. 20, 201, 204, 374 (1929)—C.A. 24, 1732.
61. G. W. Ayers, Jr., to Pure Oil Co., U.S. pat. 2,420,218 (1947)—C.A. 41, 7105.
62. G. W. Ayers, Jr., and D. M. Barton to Pure Oil Co., U.S. pat. 2,405,872 (1946)—C.A. 40, 6805.
63. G. W. Ayers, Jr., D. M. Barton, and E. E. Harton to Pure Oil Co., U.S. pat. 2,417,041 (1947)—C.A. 41, 7103.
64. G. W. Ayers, Jr., D. C. Bond, and L. M. Henderson to Pure Oil Co., U.S. pat. 2,315,384 (1943)—C.A. 37, 5855.
65. G. W. Ayers, Jr., and L. M. Henderson to Pure Oil Co., (a) U.S. pat. 2,316,753 (1943); 2,360,537 (1944); 2,373,004 (1945); (b) 2,381,859 (1945)—C.A. 37, 6120; 39, 1533, 4470, 5450.
66. G. W. Ayers, Jr., and Priscilla Lyon to Pure Oil Co., U.S. pat. 2,435,732 (1948)—C.A. 42, 7015.
67. H. J. Backer, Rec. trav. chim., 54, 205-7, 215-8 (1935)—C.A. 29, 2915, 2914.
68. H. J. Backer and P. L. Stedehouder, Rec. trav. chim., 52, 437-53 (1933)—C.A. 27, 5055.
69. R. F. Bacon and W. A. Hamor, *The American Petroleum Industry*, New York, McGraw-Hill Book Co., 1916.
70. Z. M. Bacq, Bull. acad. roy. med. Belg., [6] 7, 500-27 (1942)—C.A. 38, 6390.
71. D. E. Badertscher, D. J. Crowley, and C. F. Feasley to Socony-Vac. Oil Co., U.S. pat. 2,386,773 (1945)—C.A. 40, 585.
72. Badische Anilin-u. Soda Fabrik, Ger. pat. 211,239 (1909)—C. 1909, II, 666.
73. Badische Anilin-u. Soda Fabrik (Rudolf Wietzel and Martin Luther), Ger. pat. 411,389 (1925)—C. 1925, II, 119.
74. B. Bagshawe and R. J. Truman, Analyst, 72, 189-92 (1947)—C.A. 41, 5051.

75. C. M. Bair, Jr., to Petrolite Corp., U.S. pat. 2,281,347 (1942)—C.A. 36, 6004.
76. W. E. Bakes, J. G. King, and F. S. Sinnatt, Review of Sulfur Compounds in Water-Gas and Their Removal, New York, British Library of Information, 35 p.—Chem. Met. Eng., 38, 725 (1931).
77. Balard, Ann. chim. phys., [3] 12, 294–330 (1844).
78. J. S. Ball, U.S. Bur. Mines, Rept. Investigations, 3591, 60 p. (1942)—C.A. 36, 1763.
79. J. S. Ball, G. U. Dinneen, J. R. Smith, C. W. Bailey, and Robin Van Meter, Ind. Eng. Chem., 41, 581–7 (1949)—C.A. 43, 4453.
80. J. S. Ball and W. E. Haines, Chem. Eng. News, 24, 2765–9 (1946); 25, 27 (1947)—C.A. 41, 946.
81. S. A. Ballard, K. E. Furman, and H. DeV. Finch to Shell Dev. Co., U.S. pat. 2,572,238 (1951)—C.A. 46, 5075.
82. W. P. Ballard, N. A. Merritt, and J. C. D. Oosterhout, Ind. Eng. Chem., 41, 2856–60 (1949)—C.A. 44, 1683.
83. W. P. Ballard and A. R. Vander Ploeg, Petroleum Engr., 22c, No. 5, 70–4 (1950)—C.A. 44, 6612.
84. Eugene Bamberger and E. Kraus, Ber., 29, 272–86 (1896).
85. R. A. Bannerot to Shell Dev. Co., U.S. pat. 2,245,317 (1941)—C.A. 35, 6438.
86. Jean W. Barnett, J. Chem. Soc., 1944, 5–8—C.A. 38, 2010.
- 86.5. R. J. Barnett and A. M. Seligman, J. Natl. Cancer Inst., 14, 769–803 (1954); Science, 116, 323–7 (1952)—C.A. 48, 5909, 8832.
87. E. S. G. Barron and Veronica Flood, J. Gen. Physiol., 33, 229–41 (1950)—C.A. 44, 3058.
88. E. S. G. Barron, Zelma B. Miller and G. Kalnitsky, Biochem. J., 41, 62–8 (1947)—C.A. 41, 4774.
89. J. M. Barron, A. R. Vander Ploeg, and Hubert McReynolds, Ind. Eng. Chem., 41, 2687–90 (1949)—C.A. 44, 2214.
90. R. Baynes, J. Fearenside, and W. P. Thomson, Ger. pat. 30,610 (1884).
91. L. C. Beard, Jr., Oil Gas J., 28, No. 42, 130, 276 (1930).
92. D. J. Beaver and M. C. Throdahl, Rubber Chem. Technol., 17, 896–902 (1944)—C.A. 39, 2424.
93. A. E. Becker to S. O. Dev. Co., U.S. pat. 1,676,724 (1928)—C.A. 22, 3289.
94. H. Beckurts and Robert Otto, Ber., 11, 2065–6 (1878).
95. C. W. Bedford and L. B. Sebrell, Ind. Eng. Chem., 14, 25–31 (1922)—C.A. 16, 855.

96. F. B. Behrens to U. O. Prods. Co., U.S. pat. 1,927,147 (1933)—C.A. 27, 5961.
97. Arnold Belchetz to Shell Dev. Co., U.S. pat. 2,055,423 (1936)—C.A. 30, 7835.
98. Arnold Belchetz and B. R. Carney to Shell Dev. Co., U.S. pat. 2,085,523 (1937)—C.A. 31, 5990.
99. F. W. Bell, L. L. Lovell, and A. E. Martin to Shell Dev. Co., Brit. pat. 570,863 (1945)—C.A. 40, 6806.
100. R. T. Bell to Pure Oil Co., (a) U.S. pat. 2,354,646 (1944); (b) 2,430,269 (1947)—C.A. 38, 6541; 42, 1731.
101. R. T. Bell and M. S. Argruss, Ind. Eng. Chem., Anal. Ed., 13, 297-9 (1941)—C.A. 35, 4706.
102. E. H. Bender to Phillips Petroleum Co., U.S. pat. 2,373,645 (1945)—C.A. 39, 4469.
103. R. O. Bender to Sinclair Refg. Co., U.S. pat. 2,272,594, 2,272,595, 2,272,596 (1942); Reissues, 22,135, 22,136 and 22,137 (1942)—C.A. 36, 3953; 37, 759.
104. W. L. Benedict to U. O. Prods. Co., (a) U.S. pat. 1,971,172 (1934); (b) 2,102,878 (1937); 2,138,566 (1938); (c) 2,253,011 (1941); (d) 2,291,276 (1942); (e) 2,297,866 (1942); (f) 2,317,600 (1943)—C.A. 28, 6295; 32, 1443; 33, 2322; 35, 8279; 37, 1259, 1859, 6447.
105. W. L. Benedict and J. E. Ahlberg to U. O. Prods. Co., U.S. pat. 2,273,012 (1942)—C.A. 36, 3953.
106. W. L. Benedict and C. G. Dryer to U. O. Prods. Co., U.S. pat. 2,270,248 (1942)—C.A. 36, 3954.
107. W. L. Benedict and C. Wirth, III, U.S. pat. 2,013,400 (1935)—C.A. 29, 7064.
108. R. C. Benner and A. P. Thompson to Gen. Chem. Co. of N. Y., U.S. pat. 1,778,517 (1930)—C.A. 24, 5950.
109. G. M. Bennett, J. Chem. Soc., 119, 418-25 (1921)—C.A. 15, 2061.
110. H. T. Bennett to Mid-Continent Petroleum Corp., U.S. pat. 1,965,821 (1934)—C.A. 28, 5657.
111. H. T. Bennett, H. H. Hopkins and J. R. Marshall to Mid-Continent Petroleum Corp., U.S. pat. 2,026,492 (1935)—C.A. 30, 1218.
112. H. T. Bennett and LeR. G. Story, Oil Gas J., 27, No. 48, 162 (1927)—C.A. 21, 2979.
113. H. T. Bennett, Le R. G. Story and I. A. Clark, Oil Gas J., 25, No. 47, 138 (1927)—C.A. 21, 2786.
114. M. Benson, (a) Brit. pat. 170,093 (1920); (b) U.S. pat. 1,607,043 (1926)—C.A. 16, 1148; 21, 317.

115. R. D. Bent and J. H. McCullough, *Oil Gas J.*, 47, No. 19, 95-103 (1948)—C.A. 43, 381.
116. R. D. Bent and C. A. Pines to The Atlantic Refg. Co., U.S. pat. 2,340,922 (1944)—C.A. 38, 4792.
117. L. I. Berents and A. V. Frost, *Compt. rend. acad. sci., URSS*, 29, 196-8 (1940)—C.A. 35, 4188.
118. Clyde Berg, W. E. Bradley, R. I. Stirton, R. G. Fairfield, C. B. Leffert, and J. H. Ballard, *Chem. Eng. Progress*, 1, No. 1; *Trans. Am. Inst. Chem. Engrs.*, 43, 1-12 (1947)—C.A. 41, 2230.
119. F. Berg, (a) U.S. pat. 560,463 (1896); (b) 736,479 (1903).
120. C. W. Berger, (a) *Refiner Natural Gasoline Mfr.*, 14, 470-2 (1935); (b) *ibid.*, 15, 411-12 (1936); (c) *ibid.*, 16, 136-40 (1937); *Natl. Petroleum News*, 29, No. 11, 152-6 (1937); *Oil Gas J.*, 35, No. 43, 81-2 (1937)—C.A. 29, 8303; 31, 5553, 7237, 5557.
121. C. W. Berger to Globe Oil Refg. Co., (a) U.S. pat. 2,318,582 (1943); (b) 2,334,378 (1943)—C.A. 37, 6447; 38, 3826.
122. L. B. Berger, M. A. Elliott, J. C. Holtz, and H. S. Schrenk, U.S. Bureau Mines, *Rept. of Investigations*, 3713, 13 p. (1943)—C.A. 37, 6843.
123. Friedrich Bergius, U.S. pat. 1,344,671 (1920)—C.A. 14, 2550.
124. Friedrich Bergius and A. G. f. Petroleum ind., Nürnberg, Ger. pat. 290,563 (1913)—C. 1916, I, 647.
125. Friedrich Bergius and John Billwiller, Ger. pat. 301,231 (1919)—C. 1920, II, 374.
126. Ernst Bergmann and David Wagenberg, Ber., 63, 2585-92 (1930)—C.A. 25, 1239.
127. Hilding Bergström and K. G. Trobeck, *Svensk Papperstidn.*, 42, 554-7 (1939)—C.A. 34, 1171.
128. A. G. V. Berry, Brit. pat. 428,542 (1935)—C.A. 29, 6692.
129. Theodor Bersin, *Biochem. Z.*, 245, 466-72 (1932)—C.A. 26, 3175.
130. A. Bertram, Ber., 25, 63 (1892).
131. I. E. Bepolov and A. Degtyareva, *Azerbaidzhanskoe Neftyanoe Khozyaistyo*, 1931, Nos. 11-12, 88-90—C.A. 26, 2309.
132. E. E. C. G. Beyer and Peter von Ditmar, Ger. pat. 387,592 (1923)—C. 1924, II, 139R.
133. Silvio Bezzi, *Gaz. chim. ital.*, 65, 693-703, 704-23 (1935)—C.A. 30, 2171.

- 133.5. A. F. Bickel and E. C. Kooijman, *Nature*, **170**, 211-2 (1952)—C.A. **48**, 1944.
134. C. F. Bickford, W. S. Jones, and J. S. Keene, *J. Am. Pharm. Assoc., Sci. Ed.*, **37**, 255-61 (1948)—C.A. **42**, 8703.
135. E. C. Billheimer and E. E. Reid, *J. Am. Chem. Soc.*, **52**, 4338-44 (1930)—C.A. **25**, 75.
136. A. Binz, C. R  th, and E. Walter, *Ber.*, **57**, 1398-1403 (1924).
137. A. E. Birch to Atlantic Refg. Co., U.S. pat. 2,082,787 (1937)—C.A. **31**, 5564.
138. S. F. Birch, *Oil Gas J.*, **28**, No. 1, 190, 193-4; No. 2, 38, 108, 170, 172, 174 (1929)—C.A. **23**, 4055.
139. S. F. Birch and W. S. G. P. Norris, (a) *J. Chem. Soc.*, **127**, 898-907 (1925); (b) *Ind. Eng. Chem.*, **21**, 1087-90 (1929)—C.A. **19**, 2407; **24**, 493.
140. S. F. Birch and W. S. G. P. Norris, *J. Chem. Soc.*, **127**, 1934-44 (1925); *Oil Gas J.*, **24**, No. 28, 148, 150, 152-6 (1925); *Refiner Natural Gasoline Mfr.*, **7**, No. 7, 94, 96, 98 (1928)—C.A. **20**, 278, 2582; **23**, 1742.
141. S. F. Birch and W. S. G. P. Norris, *Trans. Fuel Conference, World Power Conference, London*, **1928**, 1, 641-8 (1929); *Oil Gas J.*, **28**, No. 8, 46, 162, 164, 166, 168 (1929)—C.A. **23**, 4805, 4809.
142. S. F. Birch and R. Stansfield, *Ind. Eng. Chem.*, **28**, 668-72 (1936)—C.A. **30**, 5401.
143. E. R. Birkhimer to Atlantic Refg. Co., *Can. pat.* 419,942 (1944); U.S. pat. 2,345,449 (1944)—C.A. **38**, 3813, 4792.
144. A. P. Bjerregaard, *Oil Gas J.*, **23**, No. 40, 96, 172, 180 (1925)—C.A. **19**, 1491.
145. A. P. Bjerregaard, U.S. pat. 1,791,521 (1931)—C.A. **25**, 1986.
146. A. P. Bjerregaard to Doherty Research Co., U.S. pat. 1,761,810 (1930)—C.A. **24**, 3639.
147. J. C. Black to S. O. Co., U.S. pat. 968,640 (1910)—C.A. **4**, 3002.
148. J. C. Black to Richfield Oil Co. of Calif., U.S. pat. 1,749,240 (1930)—C.A. **24**, 2285.
149. J. C. Black and M. L. Chappell to Pan Amer. Pet. Co., U.S. pat. 1,710,143, 1,710,200, 1,710,201 (1929)—C.A. **23**, 2818, 2819.
150. J. C. Black and W. H. Low to Pan Amer. Pet. Co., U.S. pat. 1,696,377 (1928)—C.A. **23**, 968.

151. J. C. Black and J. R. McConnell to Richfield Oil Co. of Calif., U.S. pat. 1,759,730 (1930)—C.A. 24, 3638.
152. J. C. Black, W. D. Rial, and R. T. Howes, U.S. pat. 1,592,329 (1926)—C.A. 20, 3234.
153. Stanley Blackburn and Frederick Challenger, J. Chem. Soc., 1938, 1872-8—C.A. 33, 1265.
154. H. S. Blackmore, Belg. pat. 179,502 (1904); Fr. pat. 346,275 (1904); Brit. pat. 19,744 of 1904; U.S. pat. 770,214 (1904); 793,026 (1905); 809,086 (1906); Ger. pat. 187,650 (1905)—J. Soc. Chem. Ind., 24, 127, 613 (1905); 22, 930 (1904); 25, 117 (1906); C.A. 2, 731.
155. H. S. Blackmore to Black-Ford Utility Oil Co., U.S. pat. 809,087 (1906)—J. Soc. Chem., Ind., 25, 117 (1906).
156. M. Blagodarov, Novosti Tekhniki, 1939, No. 16, 33-4—C.A. 34, 875.
157. C. M. Blair, Jr., and I. S. Boydston to Petrolite Corp., U.S. pat. 2,208,505, 2,208,506, 2,208,507, 2,208,508, 2,208,509, 2,208,510 (1940)—C.A. 35, 612.
158. W. F. Bland, Petroleum Processing, 5, 351-5; Petroleum Refiner, 29, No. 4, 128-30 (1950)—C.A. 44, 6610.
159. W. F. Bleecker, (a) U.S. pat. 1,794,668 (1931); 1,862,952 (1932); (b) 1,837,519 (1931)—C.A. 25, 2278; 26, 4166, 1201.
160. G. Blieberger, U.S. pat. 1,158,367 (1915)—C.A. 9, 3353.
161. E. Blümner, U.S. pat. 1,573,370 (1926)—C.A. 20, 1512.
162. Henry Blumenberg, Jr., (a) U.S. pat. 1,649,384 (1927); (b) 1,713,250, 1,713,251, 1,713,252 (1929); 1,734,197 (1930)—C.A. 22, 498; 23, 3316, 3340; 24, 495.
163. Henry Blumenberg, Jr., and A. M. Buley, Can. pat. 280,816 (1928)—C.A. 22, 3041.
164. J. S. Bogen and V. Haensel, Proc. Mid-Year Meeting, Am. Petroleum Inst. 30M (III), 319-62 (1950)—C.A. 45, 3150.
165. S. I. Bolko, B. A. Englin, and N. A. Chuvikova, Nef-tyanoe Khoz., 18, No. 8, 20-3 (1937)—C.A. 32, 7707.
166. J. A. Bolt to S. O. Co. of Ind., U.S. pat. 2,413,945 (1947)—C.A. 41, 1422.
167. J. A. Bolt and B. H. Shoemaker to S. O. Co. of Ind., U.S. pat. 2,232,048 (1941)—C.A. 35, 3809.
168. E. K. Bolton to Canadian Ind. Ltd., Can. pat. 431,359 (1945)—C.A. 40, 1352.
169. D. C. Bond, Oil Gas J., 44, No. 31, 83-91 (1945)—C.A. 40, 1011.

170. D. C. Bond to Pure Oil Co., (a) U.S. pat. 2,316,759 (1943); (b) 2,369,771 (1945); 2,425,414 (1947); (c) 2,427,250 (1947); (d) 2,494,687 (1950); (e) 2,535,833 (1950)—C.A. 37, 6120; 39, 5466; 41, 7736, 7738; 46, 4560, 2288.
171. D. C. Bond, G. W. Ayers, Jr., and L. M. Henderson to Pure Oil Co., U.S. pat. 2,314,919 (1943)—C.A. 37, 5582.
172. D. C. Bond and N. B. Russell to Pure Oil Co., U.S. pat. 2,447,051 (1948)—C.A. 42, 7970.
173. G. R. Bond, Jr., Ind. Eng. Chem., Anal. Ed., 5, 257–60 (1933)—C.A. 27, 4192.
174. A. J. Boote and H. G. W. Kittredge, U.S. pat. 620,882 (1899).
175. L. E. Border, Oil Gas J., 39, No. 10, 36–8, 40; No. 26, 55, 56 (1940); Chem. Met. Eng., 47, 776–8 (1940)—C.A. 35, 3071, 2308, 3071.
176. L. E. Border to Shell Dev. Co., (a) U.S. pat. 2,267,809 (1941); (b) 2,315,480 (1943); (c) 2,315,766 (1943); (d) 2,337,225 (1943); 2,358,619 (1944); (e) Brit. pat. 557,315 (1943)—C.A. 36, 3039; 37, 5856; 38, 3825; 39, 1756, 3154.
177. J. N. Borglin and Emil Ott to Hercules Powder Co., U.S. pat. 2,076,875 (1937)—C.A. 31, 4017.
178. Parry Borgstrom, Ind. Eng. Chem., 22, 249–50, 250–3 (1930)—C.A. 24, 3892–3.
179. Parry Borgstrom to L. L. Reeves, U.S. pat. 1,840,269 (1932)—C.A. 26, 1428.
180. Parry Borgstrom, R. W. Bost, and J. C. McIntire, Ind. Eng. Chem., 22, 87–9 (1930)—C.A. 24, 1208.
181. Parry Borgstrom, V. Dietz, and E. E. Reid, Ind. Eng. Chem., 22, 245–7 (1930)—C.A. 24, 3893.
182. Parry Borgstrom, L. M. Ellis, Jr., and E. E. Reid, J. Am. Chem. Soc., 51, 3649–51 (1929)—C.A. 24, 335.
183. Parry Borgstrom and J. G. McIntire, Ind. Eng. Chem., 22, 253–5 (1930)—C.A. 24, 3893.
184. Parry Borgstrom and E. E. Reid, Ind. Eng. Chem., Anal. Ed., 1, 186–7 (1929)—C.A. 23, 5439.
185. Parry Borgstrom, R. Roseman, and E. E. Reid, Ind. Eng. Chem., 22, 248–9 (1930)—C.A. 24, 3892.
186. W. Borsche and W. Lange, Ber., 39, 2346–56 (1906).
187. E. A. Bosing to Buffalo Electro-Chemical Co., Inc., U.S. pat. 1,951,324 (1934)—C.A. 28, 3574.
188. E. Bosshard and W. Wildi, Helv. chim. acta, 13, 572–86 (1930)—C.A. 24, 4923.

- 188.5. R. W. Bost, P. K. Starnes, and E. L. Wood, *J. Am. Chem. Soc.*, **73**, 1968-70 (1951)—C.A. **46**, 927.
189. R. W. Bost, J. O. Turner, and M. W. Conn, *J. Am. Chem. Soc.*, **55**, 4956-7 (1933)—C.A. **28**, 753.
190. R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, **54**, 1985-7 (1932)—C.A. **26**, 3230.
191. V. A. Botnikov, L. D. Nersesov, and K. K. Fishman, *Vostochnaya Neft*, **1949**, No. 9, 34-6.
192. F. H. Bottomley to Gray Process Corp., U.S. pat. 2,312,020 (1943)—C.A. **37**, 4890.
193. Harold Bottomley, (a) *Refiner Natural Gasoline Mfr.*, **15**, 359-62 (1936); (b) *ibid.*, **20**, 526-9 (1941); *Oil Gas J.*, **40**, No. 24, 37, 38 (1941); (c) *Natl. Petroleum News*, **32**, No. 42, R330-3 (1941)—C.A. **31**, 5142; **36**, 1474, 4699, 885.
194. Joseph Bougault, Eugene Cattelain, and Pierre Chabrier, *Compt. rend.*, **208**, 657-9 (1939); *Bull. soc. chim.*, [5] **7**, 781-9 (1940)—C.A. **33**, 4580; **36**, 2198.
195. Louis Bourdelles, *Fr. pat.* 632,378 (1926)—C.A. **22**, 3523.
196. Wesley Bourne, *J. Pharmacol.*, **28**, 409-32 (1926); *Anesthesia and Analgesia*, **6**, 131-40 (1927)—C.A. **20**, 3747; **21**, 3981.
197. G. A. Boyd, *Oil Gas J.*, **32**, No. 8, 16, 31 (1933)—C.A. **27**, 5525.
198. G. A. Boyd to S. O. Co. of Ind., U.S. pat. 2,242,387 (1941)—C.A. **35**, 6104.
199. J. Bragg, U.S. pat. 604,515 (1898).
200. R. C. Brandon to S. O. Dev. Co., U.S. pat. 2,436,550 (1948)—C.A. **42**, 3560.
201. P. L. Brandt and J. O. Hougen, *Oil Gas J.*, **37**, No. 46, 98, 100, 103 (1939)—C.A. **33**, 8967.
202. R. L. Brandt, *Ind. Eng. Chem.*, **22**, 218-23 (1930)—C.A. **24**, 1962.
203. Karl Braus to I. G. Farben., U.S. pat. 1,916,824 (1933)—C.A. **27**, 4656.
204. U. B. Bray to Union Oil Co. of Calif., U.S. pat. 2,183,782 (1941)—C.A. **34**, 2585.
205. A. Brin and L. Q. Brin, *Brit. pat.* 10,968 of 1886.
206. British Celanese, Ltd., *Brit. pat.* 494,214 (1938)—C.A. **33**, 2539.
207. H. J. Broderson to S. O. Co. of Ind., U.S. pat. 1,698,428 (1929)—C.A. **23**, 1260.

208. B. T. Brooks, *Ind. Eng. Chem.*, **16**, 588 (1924)—C.A. **18**, 2803.
209. B. T. Brooks and I. W. Humphrey, *J. Am. Chem. Soc.*, **40**, 822–56 (1918)—C.A. **12**, 1643.
210. B. T. Brooks and H. O. Parker, U.S. pat. 1,528,398 (1925)—C.A. **19**, 1494.
211. J. A. Brooks, J. H. Krause, T. B. Tom, and Nathan Fragen to S. O. Co. of Ind., U.S. pat. 2,556,414 (1951)—C.A. **46**, 1024.
212. G. M. Brooner and M. W. Conn, *Oil Gas J.*, **45**, No. 25, 96–8, 115–21 (1946)—C.A. **41**, 270.
213. A. S. Broun and E. M. Zelenina, *J. Applied Chem. (USSR)*, **13**, 1491–7 (1940)—C.A. **35**, 4188.
214. P. V. Brower to Shell Dev. Co., U.S. pat. 2,228,028 (1941)—C.A. **35**, 3075.
215. P. V. Brower and Lowry Love to Shell Dev. Co., U.S. pat. 2,311,328 (1943)—C.A. **37**, 4890.
216. C. L. Brown, Alexis Voorhies, Jr., and W. M. Smith, *Ind. Eng. Chem.*, **38**, 136–40 (1946)—C.A. **40**, 2611.
217. E. S. Brown and D. B. Nutt to S. O. Co. of Ind., U.S. pat. 2,049,423 (1936)—C.A. **30**, 6546.
218. K. M. Brown, *World Petroleum*, **18**, No. 8, 72–4 (1947)—C.A. **41**, 7087.
219. K. M. Brown and C. G. Gerhold to U. O. Prods. Co., U.S. pat. 2,437,348 (1948)—C.A. **42**, 7975.
220. R. H. Brownlee, U.S. pat. 1,309,432 (1919)—C.A. **13**, 2274.
221. Horst Brückner, *Chem. Fabrik.*, **1939**, 489–93—C.A. **34**, 872.
222. W. Bruening, U.S. pat. 421,904 (1890).
223. H. A. Bruson to Röhm and Haas Co., U.S. pat. 2,282,931 (1942)—C.A. **36**, 6301.
224. André Bruzac, (a) Fr. pat. 684,618 (1929); 689,021 (1930); 693,281 (1929); (b) 752,690 (1933); (c) 764,813, 770,677 (1934)—C.A. **24**, 5305; **25**, 1060, 1666; **28**, 979, 5767; **29**, 691.
225. K. Bube, *Brit. pat.* 260,129 (1925)—C.A. **21**, 3454.
226. A. E. Buell to Phillips Petroleum Co., U.S. pat. 2,094,485 (1937); *Can. pat.* 371,482 (1938)—C.A. **31**, 8912; **32**, 2729.
227. A. E. Buell and W. A. Schulze to Phillips Petroleum Co., (a) U.S. pat. 2,016,272 (1935); (b) 2,016,271 (1935); 2,075,171, 2,075,172, 2,075,173, 2,075,174 (1937); (c) 2,098,943 (1937)—C.A. **29**, 8312; **31**, 3679; **32**, 337.

228. T. Bullinger, M. Melhardt, H. Weisz, H. Winternitz, and E. Zerner, Brit. pat. 218,989 (1923)—C.A. 19, 575.
229. F. C. Bunge and Heinrich Macura, Fr. pat. 633,643 (1928); Brit. pat. 285,000 (1927)—C.A. 22, 3519, 4779.
230. N. Bunge, Ber., 3, 911-3 (1870).
231. A. H. Burchard, Brit. pat. 24,216 of 1909; 20,982 of 1910—J. Soc. Chem. Ind., 30, 123 (1911).
- 231.5. A. B. Burg and R. I. Wagner, J. Am. Chem. Soc., 76, 3307-10 (1954)—C.A. 49, 10166.
232. Louis Burgess, Trans. Am. Electrochem. Soc., 49 (preprint) (1926)—C.A. 20, 1512.
233. Louis Burgess to S. O. Dev. Co., (a) U.S. pat. 1,681,638 (1928); (b) 1,681,895 (1928)—C.A. 22, 3984.
234. R. E. Burk to S. O. Co. of Ohio, (a) U.S. pat. 2,009,954 (1935); (b) 2,033,877 (1936); (c) 2,201,883 (1940); (d) 2,306,933 (1942); (e) 2,343,841 (1944)—C.A. 29, 6413; 30, 3223; 34, 6807; 37, 3970; 38, 3814.
235. R. E. Burk and E. C. Hughes to S. O. Co. of Ohio, (a) U.S. pat. 2,020,932 (1935); (b) 2,162,670 (1939), 2,232,436 (1941); (c) 2,150,149 (1939); (d) 2,301,802 (1942); (e) 2,401,334 (1946)—C.A. 30, 607; 33, 8004; 35, 3809; 33, 4776; 37, 2566; 41, 5297.
236. A. M. Burke and S. Wright, U.S. pat. 65,999 (1867).
237. G. H. Burruss to Col-Tex Refg. Co., U.S. pat. 1,863,967 (1932)—C.A. 26, 4465.
238. A. W. Burwell and L. O. Sherman to L. O. Sherman, U.S. pat. 738,656 (1903).
239. N. A. Butkov and K. P. Lavrovskii, Vostochnaya Neft., 1939, No. 1, 28-36—C.A. 34, 7589.
240. J. G. Butz, U.S. pat. 2,222,400 (1940)—C.A. 35, 2313.
241. A. C. Byrns to Union Oil Co. of Calif., (a) U.S. pat. 2,309,337 (1943); (b) Can. pat. 413,254 (1943); U.S. pat. 2,325,033, 2,325,034 (1943); (c) 2,369,432 (1945); 2,398,919 (1946)—C.A. 37, 4238, 5562; 38, 246; 39, 5451; 40, 4209.
242. A. C. Byrns, W. E. Bradley, and M. W. Lee, Ind. Eng. Chem., 35, 1160-7 (1943)—C.A. 37, 6863.
- 242.5. T. L. Cairns, G. L. Evans, A. W. Larchar, and B. C. McKusick, J. Am. Chem. Soc., 74, 3982-9 (1952)—C.A. 47, 4283.
243. W. S. Calcott and I. E. Lee to Du Pont Co., U.S. pat. 1,785,513 (1930)—C.A. 25, 483.
244. Lyle Caldwell to Celite Co., (a) U.S. pat. 1,691,266 (1928); (b) 1,802,628 (1931)—C.A. 23, 509; 25, 3820.

245. F. L. Campbell, W. N. Sullivan, L. E. Smith, and H. L. J. Haller, *J. Econ. Entomol.*, **27**, 1176–85 (1934)—C.A. **29**, 3101.
246. J. A. Campbell, Jr., and T. M. Phillips to Union Oil Co., U.S. pat. 2,143,405 (1939)—C.A. **33**, 3133.
247. Canadian-American Finance and Trading Co., Ltd., Fr. pat. 521,630 (1921)—C. **1923**, IV, 36.
248. R. F. Cane, *Australian Chem. Inst. J. & Proc.*, **10**, 279–86 (1943)—C.A. **38**, 1465.
249. H. H. Cannon to Cannon-Prutzman Treating Processes, Ltd., (a) Brit. pat. 367,969 (1930); U.S. pat. 1,798,784 (1931); 1,888,219 (1932); 1,926,226 (1933); 1,979,448 (1934); (b) 1,924,911 (1933)—C.A. **27**, 2294; **25**, 3159; **27**, 1502, 5959; **29**, 329; **27**, 5531.
250. H. H. Cannon and W. W. Gary to Cannon-Prutzman Treating Processes, Ltd., U.S. pat. 1,789,167, 1,789,168 (1931); 1,907,150 (1933)—C.A. **25**, 1067; **27**, 3600.
251. R. G. Capell and R. C. Amero to Floridin Co., U.S. pat. 2,433,426 (1947)—C.A. **42**, 2095.
252. L. Carius, *Ann.*, **124**, 221–42 (1862).
253. P. J. Carlisle to Du Pont Co., U.S. pat. 2,058,131 (1936)—C.A. **31**, 248.
254. P. J. Carlisle to Roessler & Hasslacher Chem. Co., Can. pat. 300,843 (1930); 311,328 (1931); U.S. pat. 1,801,412 (1931)—C.A. **24**, 3639; **25**, 3357.
255. P. J. Carlisle and C. R. Harris to Roessler & Hasslacher Chem. Co., U.S. pat. 1,862,003 (1932)—C.A. **26**, 4167.
256. F. J. Carman, U.S. pat. 501,988 (1903).
257. W. M. Carney, H. D. Noll, and A. W. Hoge, *Petroleum Engr.*, **20**, No. 2, 246–50 (1948); *Petroleum Times*, **52**, 974–6 (1948); *Petroleum Refiner*, **27**, No. 12, 625–8 (1948); *Petroleum Processing*, **3**, 1267–9 (1948); *World Petroleum*, **19**, No. 13, 49–51 (1948)—C.A. **43**, 841, 3180.
- 257.5. Cesare Carola, *Olii minerali, grassi e saponi, colori e vernici*, **27**, 82–4 (1950)—C.A. **45**, 2658.
258. Georges Carteret and Maurice Davaux, Fr. pat. 573,407 (1924)—C. **1925**, I, 2131.
259. A. V. Caselli and A. C. Nixon to Shell Dev. Co., (a) U.S. pat. 2,258,279 (1941); (b) 2,270,667 (1942); (c) 2,285,898 (1942)—C.A. **36**, 893, 3954, 7295.
260. L. J. Catlin, *Refiner Natural Gasoline Mfr.*, **7**, No. 2, 66–8 (1928); **9**, No. 4, 67, No. 5, 95, No. 6, 77, No. 7, 117, No. 8, 99 (1930)—C.A. **24**, 5140.

261. W. E. Catlin to Du Pont Co., U.S. pat. 2,284,637 (1942)—C.A. 36, 6707.
262. R. A. Cattell, H. P. Wheeler, Jr., et al., U.S. Bur. Mines, Inform. Circ., 7358, 29 p. (1946)—C.A. 40, 6241.
263. S. P. Cauley to Socony-Vac. Oil Co., (a) U.S. pat. 2,455,656 (1948); (b) 2,467,355 (1949); (c) 2,446,507 (1948)—C.A. 43, 1557, 6235, 8667.
264. C. J. Cavallito, *J. Biol. Chem.*, 164, 29–34 (1946)—C.A. 41, 94.
265. C. M. Cawley and C. C. Hall, *J. Soc. Chem. Ind.*, 62, 116–9 (1943)—C.A. 37, 6640.
266. Cela Holding S. A., Brit. pat. 454,036 (1936)—C.A. 31, 1658.
267. Frederick Challenger, *Ind. Chemist*, 2, 445–8 (1926)—C.A. 21, 646.
268. Frederick Challenger, John Haslam, and R. J. Bramhall, *J. Inst. Petr. Technologists*, 12, 106–134 (1926)—C.A. 20, 3560.
269. Frederick Challenger, John Haslam, R. J. Bramhall, and James Walkden, *Petroleum Times*, 15, 289–90, 513–6 (1926)—C.A. 20, 3231.
270. Frederick Challenger and A. A. Rawlings, *J. Chem. Soc.*, 1937, 868–75—C.A. 31, 5321.
271. C. F. Chandler, *Ind. Eng. Chem.*, 4, 132–4 (1912)—C.A. 6, 796.
272. L. V. Chaney and A. E. Buell to Phillips Petroleum Co., U.S. pat. 2,111,487 (1938)—C.A. 32, 3951.
273. L. V. Chaney and W. A. Schulze, U.S. pat. 1,998,863 (1935)—C.A. 29, 4167.
274. M. L. Chappell to S. O. Co. of Calif., U.S. pat. 1,891,619 (1932)—C.A. 27, 2028.
275. M. L. Chappell and G. J. Ziser to S. O. Co. of Calif., U.S. pat. 1,741,555 (1929)—C.A. 24, 1209.
276. M. L. Chappell, G. J. Ziser, and E. L. Moyer to S. O. Co. of Calif., U.S. pat. 1,672,304 (1928)—C.A. 22, 2661.
277. W. M. Charch, M. M. Brubaker, and F. M. Meigs to Du Pont Co., U.S. pat. 2,098,542 (1937)—C.A. 32, 352.
278. Joseph Chatt and F. G. Mann, *J. Chem. Soc.*, 1938, 1949–54—C.A. 33, 2433.
279. L. P. Chebotar to The Texas Co., U.S. pat. 2,036,396 (1936)—C.A. 30, 3626.
280. H. Cheftel, F. Custot, and M. Nowak, *Bull. soc. chim. France*, 1949, 441–3—C.A. 43, 8957.

281. Chem. Fab. Libenia, Ger. pat. 495,271 (1927)—C.A. 24, 3353.
282. Chem. Fabr. von Heyden (Walter Ohse), Ger. pat. 550,-685 (1928)—C.A. 26, 4828.
283. T. Cherchez, Mon. pétrole roumain, 1946, 230-1; Chimie & industrie, 57, 569 (1947)—C.A. 42, 2749.
284. C. Cherry, U.S. pat. 15,642 (1856).
285. J. K. Chowdhury and R. C. Bagchi, J. Indian Chem. Soc., 5, 111-25 (1928)—C.A. 22, 3981.
286. J. K. Chowdhury and S. C. Das, J. Indian Chem. Soc., 7, 379-400 (1930).
287. J. C. Clancey, Can. pat. 215,380, 215,386, 215,387 (1922); U.S. pat. 1,423,710, 1,423,711, 1,423,712 (1922)—C.A. 16, 1148, 3202.
288. E. Clark, U.S. pat. 232,685 (1880).
289. L. A. Clarke to The Texas Co., (a) U.S. pat. 1,974,805 (1934); (b) 2,131,999 (1938)—C.A. 28, 7516; 33, 368.
290. R. G. Clarkson and C. J. Pedersen to Du Pont Co., U.S. pat. 2,054,282 (1936)—C.A. 30, 7731.
291. A. Claus, Ber., 8, 530-3 (1875).
292. F. G. Claussen and G. T. B. Cobbett, Brit. pat. 15,593 of 1907.
- 292.5. G. Claxton and W. H. Hoffert, J. Soc. Chem. Ind., 65, 333-41, 341-4 (1946)—C.A. 41, 1577.
293. J. O. Clayton and D. H. Etzler, J. Am. Chem. Soc., 69, 974-5 (1947)—C.A. 41, 4096.
294. L. W. Clemence and M. T. Leffler, J. Am. Chem. Soc., 70, 2439-40 (1948)—C.A. 42, 8154.
295. L. W. Clemence and M. T. Leffler to Abbott Laboratories, U.S. pat. 2,510,738, 2,510,739, 2,510,740 (1950)—C.A. 45, 175.
296. A. M. Clifford to Goodyear Tire Co., Can. pat. 321,453 (1932)—C.A. 26, 3264.
297. Oscar Codier to Bennett-Clark Co., U.S. pat. 2,042,056 (1936)—C.A. 30, 5024.
298. S. G. Cohen and D. B. Sparrow, J. Polymer Sci., 3, 693-703 (1948)—C.A. 43, 8199.
299. A. E. Cole, J. Pharmacol., 54, 448-53 (1935)—C.A. 30, 1443.
300. R. M. Cole to Shell Dev. Co., (a) U.S. pat. 2,392,579 (1946); (b) 2,394,751 (1946); (c) 2,413,312 (1946); (d) 2,431,920 (1947)—C.A. 40, 1024, 2468; 41, 1423; 42, 6107.

301. R. M. Cole and D. D. Davidson, *Ind. Eng. Chem.*, **41**, 2711-15 (1949)—*C.A.* **44**, 2216.
302. T. F. Colin, (a) U.S. pat. 607,017 (1898); (b) 685,907 (1901); (c) 744,720 (1903).
303. T. F. Colin and O. P. Amend, U.S. pat. 723,368 (1903).
304. G. Collin, T. P. Hilditch, P. Marsh, and A. F. McLeod, *J. Soc. Chem. Ind.*, **52**, 272-5T (1933)—*C.A.* **28**, 1984.
305. A. M. Collins to Du Pont Co., U.S. pat. 2,351,108 (1944)—*C.A.* **38**, 5338.
306. J. H. Collins, *Petroleum World*, **37**, No. 1, 43 (1940).
307. R. A. Collins to Hercules Powder Co., U.S. pat. 2,409,614 (1946)—*C.A.* **41**, 608.
308. Salmen Comay to U. O. Prods. Co., U.S. pat. 2,045,262 (1936)—*C.A.* **30**, 5778.
309. Compagnie français de raffinage, (a) Fr. pat. 859,311 (1940); (b) Brit. pat. 668,089 (1952)—*C.A.* **42**, 3559; **46**, 7756.
310. Compagnie générale industrielle, Fr. pat. 644,281 (1927)—*C.A.* **23**, 1748.
311. Compagnie des Mines de Vicoigne, Noeux et Drocourt, Fr. pat. 691,118 (1929)—*C.A.* **25**, 1068.
312. J. B. Conant and A. H. Blatt, *J. Am. Chem. Soc.*, **50**, 542-50, 551-8 (1928)—*C.A.* **22**, 943, 941.
- 312.5. W. R. Conard and C. E. Best to Firestone Tire & Rubber Co., U.S. Pat. Appl. 96,832 (1952)—*C.A.* **47**, 1981.
313. A. L. Conn and C. W. Brackin, *Ind. Eng. Chem.*, **41**, 1717 (1949).
314. M. W. Conn, (a) *Oil Gas J.*, **39**, No. 24, 40, 42, 45, 47 (1940); (b) *Refiner Natural Gasoline Mfr.*, **20**, 77-85 (1941)—*C.A.* **35**, 2307, 3422.
315. M. W. Conn to Phillips Petroleum Co., U.S. pat. 2,355,366 (1944)—*C.A.* **38**, 6543.
316. G. C. Connolly to S. O. Dev. Co., U.S. pat. 2,324,066, 2,324,067 (1943)—*C.A.* **38**, 246.
317. J. P. Conrad, *J. Am. Soc. Agron.*, **33**, 37-46 (1941)—*C.A.* **35**, 2257.
318. R. H. Cook, *Petroleum Eng.*, **2**, No. 4, 163-5 (1931)—*C.A.* **25**, 4391.
- 318.5. A. C. Cope and Eugene Farkas, *J. Org. Chem.*, **19**, 385-90 (1954)—*C.A.* **49**, 4541.
319. B. B. Corson and G. S. Monroe to U. O. Prods. Co., U.S. pat. 2,298,346, 2,298,347 (1942)—*C.A.* **37**, 1860.
320. E. Courant and V. von Richter, *Ber.*, **18**, 3178-80 (1885).

321. W. A. Craig to Richfield Oil Co. of Calif., U.S. pat. 2,080,654 (1937)—C.A. 31, 5149.
322. W. A. Craig to Vapor Treating Processes, Inc., U.S. pat. 2,104,791 (1938)—C.A. 32, 1918.
323. W. A. Craig and P. C. Rich to Richfield Oil Co., (a) U.S. pat. 2,222,170 (1940); (b) 2,297,537 (1942)—C.A. 35, 1982; 37, 1858.
324. G. S. Crandall, R. S. George, and E. M. Nygaard, U.S. pat. 2,328,709 (1943)—C.A. 38, 1247.
325. R. W. Crary and M. M. Holm, *Ind. Eng. Chem.*, 29, 1389-92 (1937)—C.A. 32, 1437.
326. Blick Crawley and R. H. Griffith, *J. Chem. Soc.*, 1938, 720-3, 2034-6—C.A. 32, 6138; 33, 3243.
327. R. H. Crosby and B. R. Carney, *Petroleum Z.*, 30, No. 11, 5-6 (1934)—C.A. 28, 4873.
328. Roy Cross, (a) *Brit. pat.* 227,084 (1923); (b) U.S. pat. 1,515,733 (1924); (c) 1,587,491 (1926); (d) 1,623,018 (1927); (e) 1,654,581 (1928)—C.A. 19, 2126, 397; 20, 2410; 21, 1704; 22, 1037.
329. Roy Cross to Cross Dev. Corp., (a) U.S. pat. 1,760,585 (1930); (b) 1,882,000 (1932)—C.A. 24, 3638; 27, 593.
330. Roy Cross to Cross Dev. Corp., (a) U.S. pat. 1,718,218 (1929); (b) 1,816,827 (1931); (c) 1,817,969 (1931); (d) 1,840,158 (1932)—C.A. 23, 4060; 25, 5552; 26, 1433.
331. Roy Cross to Cross Dev. Corp., U.S. pat. 1,782,808 (1930); 1,836,577 (1931)—C.A. 25, 411; 26, 1111.
332. Roy Cross to Cross Dev. Corp., U.S. pat. 1,805,686 (1931); 1,859,027, 1,859,028, 1,865,235 (1932)—C.A. 25, 3819; 26, 3912, 3913, 4465.
- 332.5. W. W. Crouch to Phillips Pet. Co., U.S. pat. 2,421,545 (1947)—C.A. 41, 5544.
333. T. W. Culmer to Lincoln Oil Refg. Co., (a) U.S. pat. 1,772,985 (1930); (b) 1,899,314 (1933)—C.A. 24, 5146; 27, 3066.
334. G. W. Cupit, Jr., *Refiner Natural Gasoline Mfr.*, 7, No. 4, 69-71 (1928)—C.A. 22, 2657.
335. H. T. Darlington to Oil Corp. of America, (a) U.S. pat. 1,944,170 (1934); (b) 1,944,877 (1934)—C.A. 28, 2176, 2517.
336. M. S. Darrow and L. S. Sweeney, U.S. pat. 1,903,094 (1933)—C.A. 27, 3323.
337. W. Davey, *J. Inst. Petroleum*, 33, 527-30 (1947)—C.A. 42, 2755.

338. Norman Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316-24 (1942)—*C.A.* **36**, 1836.
339. R. C. Davidson, *Petroleum Refiner*, **26**, No. 9, 663-72 (1947)—*C.A.* **42**, 9138.
340. E. R. H. Davies and J. W. Armstrong, *J. Inst. Petroleum*, **29**, 323-8 (1943)—*C.A.* **38**, 2481.
341. G. H. B. Davis to Standard-I. G. Co., U.S. pat. 2,042,298 (1936)—*C.A.* **30**, 5023.
342. J. T. Davis, U.S. pat. 671,078 (1901).
343. O. L. Davis and A. C. Nixon to Shell Dev. Co., U.S. pat. 2,364,582 (1944); 2,411,083 (1946)—*C.A.* **39**, 4469; **41**, 1083.
344. R. F. Davis to S. O. Co. of Calif., U.S. pat. 1,551,806 (1925)—*C.A.* **19**, 3372.
345. R. F. Davis to U. O. Prods. Co., U.S. pat. 1,980,189 (1934)—*C.A.* **29**, 332.
346. W. N. Davis and W. H. Hampton to S. O. Co. of Calif., Brit. pat. 301,450 (1927); U.S. pat. 1,977,717 (1934)—*C.A.* **23**, 4060; **29**, 322.
347. W. N. Davis, W. H. Hampton, and E. N. Klemgard to S. O. Co. of Calif., U.S. pat. 1,705,809 (1929)—*C.A.* **23**, 2290.
348. W. N. Davis and M. M. Holm to S. O. Co. of Calif., U.S. pat. 2,013,203 (1935)—*C.A.* **29**, 7062.
349. C. A. Day, Jr., to Richfield Oil Corp., U.S. pat. 2,084,575 (1937)—*C.A.* **31**, 5994.
350. D. T. Day, (a) U.S. pat. 826,089 (1906); 1,004,632 (1911); (b) 1,365,894 (1921); (c) 1,411,237 (1922)—*C.A.* **1**, 117; **6**, 292; **15**, 944; **16**, 1863.
351. R. B. Day to U. O. Prods. Co., (a) U.S. pat. 1,970,284 (1934); (b) 1,970,281, 1,970,282, 1,970,283 (1934); 2,058,958 (1936); (c) 2,001,185 (1935)—*C.A.* **28**, 6295; **31**, 249; **29**, 4572.
352. R. B. Day to U. O. Prods. Co., (a) U.S. pat. 2,029,757 (1936); (b) 2,055,027 (1936); (c) 2,063,491 (1936); (d) 2,189,058 (1940)—*C.A.* **30**, 1991, 7835; **31**, 846; **34**, 4562.
353. R. B. Day to U. O. Prods. Co., U.S. pat. 1,920,247, 1,920,248 (1933)—*C.A.* **27**, 4916.
354. R. B. Day to U. O. Prods. Co., U.S. pat. 1,937,873 (1933); 2,001,185 (1935); 2,063,082 (1936); Brit. pat. 409,901 (1934)—*C.A.* **28**, 1179; **29**, 4572; **30**, 7835; **28**, 6295.

355. R. B. Day to U. O. Prods. Co., (a) U.S. pat. 1,948,565 (1934); (b) 2,051,939 (1936)—C.A. 28, 2891; 30, 6938.
356. W. C. Dayhuff to S. O. Co. of Calif., U.S. pat. 2,322,617 (1943)—C.A. 38, 242.
357. R. Dean, U.S. pat. 342,500 (1886).
358. Romolo de Fazi, Brit. pat. 17,030 of 1909; 27,679 of 1911; Fr. pat. 451,382 (1912); Ger. pat. 269,348 (1912)—J. Soc. Chem. Ind., 24, 999 (1910); C.A. 8, 1871; 7, 3412; 8, 2059.
359. Romolo de Fazi, Brit. pat. 25,496 of 1911; U.S. pat. 1,108,351 (1914)—C.A. 7, 1607; 8, 3500.
360. Melvin De Groote to Tretolite Co., U.S. pat. 1,844,883 (1932)—C.A. 26, 2047.
361. Julius Dehnst, Ger. pat. 178,771 (1905); U.S. pat. 1,112,602 (1914)—C.A. 1, 2201; 8, 3856.
362. Christian Deichler and Rudolf Lesser, Ger. pat. 160,717 (1905)—C. 1905, II, 731.
363. F. T. G. Delbridge, Natl. Petr. News, 22, No. 35, 40–1 (1930).
364. Marcel Delepine and Simon Eschenbrenner, Bull. soc. chim., [4] 33, 703–11 (1923)—C.A. 17, 3161.
365. Eugène Demarçay, Bull. soc. chim., [2] 20, 132–3 (1873).
366. H. D. Demoulins and F. H. Garner, Brit. pat. 216,918 (1923)—C.A. 19, 397.
367. H. J. Dempsey to S. O. Dev. Co., U.S. pat. 2,320,223 (1943)—C.A. 37, 6885.
368. G. Deniges, Compt. rend., 108, 350–1 (1889).
369. G. H. Denison, Jr., Ind. Eng. Chem., 36, 477–82 (1944)—C.A. 38, 3461.
370. R. Denkelwater, M. A. Cook, and M. Tishler, Science, 102, 12 (1945)—C.A. 39, 3809.
371. C. F. Denney, U.S. pat. 2,105,523 (1938)—C.A. 32, 2334.
372. E. R. de Ong, Ind. Eng. Chem., 22, 836–9 (1930)—C.A. 24, 4888.
373. T. L. De Pastrovich, Riv. ital. petrol., 10, No. 1, 15–22 (1942)—C.A. 38, 3464.
374. G. F. De Ridder to Shell Dev. Co., U.S. pat. 2,356,980 (1944)—C.A. 39, 411.
375. Martin DeSimo and A. P. Brady to Shell Dev. Co., U.S. pat. 2,168,256 (1939)—C.A. 33, 9324.
376. J. J. B. Deuss, Rec. trav. chim., 27, 145–8 (1908); *ibid.*, 28, 136–41 (1909)—C.A. 2, 2552; 3, 1746.
377. Deutsche Gold- u. Silber-Scheideanstalt vorm Roessler, Fr. pat. 711,046, 711,520 (1931)—C.A. 26, 1756, 2047.

- 378. Deutsche Petroleum A. G., Ger. pat. 464,253 (1928)—C. 1928, II, 1513.
- 378.5. L. T. Devol and W. J. Ayres to Tide Water Assoc. Oil Co., U.S. pat. 2,508,817 (1950)—C.A. 46, 2288.
- 379. S. J. Dickey, U.S. pat. 1,949,786 (1934)—C.A. 28, 2891.
- 380. M. A. Dietrick and C. J. Pedersen to Du Pont Co., U.S. pat. 2,411,958, 2,411,959 (1946)—C.A. 41, 1084.
- 381. S. H. Diggs, Ind. Eng. Chem., 20, 16-7 (1928)—C.A. 22, 1032.
- 382. S. H. Diggs, J. M. McGee, and T. S. Cooke to S. O. Co. of Ind., U.S. pat. 1,858,394 (1932)—C.A. 26, 3913.
- 383. W. J. D. van Dijk to Shell Dev. Co., U.S. pat. 2,160,607 (1939)—C.A. 33, 7547.
- 384. R. A. Dinerstein, J. Am. Chem. Soc., 73, 1357 (1951)—C.A. 45, 9483.
- 385. G. U. Dinneen, C. W. Bailey, J. R. Smith, and J. S. Ball, Anal. Chem., 19, 992-8 (1947)—C.A. 42, 3941.
- 386. Peter von Ditmar, U.S. pat. 1,448,643 (1923); Brit. pat. 191,037 (1922)—C.A. 17, 1886; C. 1923, II, 1131.
- 387. Egbert Dittrich, (a) Brennstoff-Chem., 14, 283-4 (1933); *ibid.*, 15, 148-9 (1934); (b) *ibid.*, 20, 348-9 (1939)—C.A. 27, 5933; 28, 5806; 34, 7779.
- 388. Leonard Dobbin, J. Chem. Soc., 57, 641 (1890).
- 389. F. J. Dobrovolsky to Roessler and Hasslacher Chem. Co., U.S. pat. 1,905,817 (1933)—C.A. 27, 3542.
- 390. C. E. Dolbear to Philip Wiseman, P. K. Wiseman, and C. E. Dolbear as Trustees, (a) U.S. pat. 2,034,712 (1936); (b) 2,090,190 (1937); (c) 2,221,183 (1940)—C.A. 30, 3215; 31, 7239; 35, 1982.
- 391. C. E. Dolbear and Philip Wiseman, U.S. pat. 2,154,424 (1939)—C.A. 33, 5641.
- 392. B. F. Dooley, Jr., to The Texas Co., U.S. pat. 1,926,515 (1933); 2,022,558 (1935)—C.A. 27, 5961; 30, 851.
- 393. A. B. Doran to Dorex Corp., U.S. pat. 2,314,576 (1943)—C.A. 37, 5581.
- 394. J. L. Dorman to Basic Patents Corp., U.S. pat. 1,828,734 (1931)—C.A. 26, 839.
- 395. I. B. Douglass and T. B. Johnson, J. Am. Chem. Soc., 60, 1486-9 (1938)—C.A. 32, 5777.
- 396. D. B. Dow, Bur. of Mines, Repts. of Investigations, No. 2191, 4 p. (1920); No. 2462, 13 p. (1923); Natl. Petroleum News, 15, No. 20, 99-111 (1920)—C.A. 16, 1313; 17, 2638, 2360.

397. Dow Chem. Co., Brit. pat. 401,210 (1933)—C.A. 28, 2363.
398. W. F. Downs, U.S. pat. 1,568,812, 1,568,813 (1926)—C.A. 20, 661.
399. T. Drake, U.S. pat. 471,963 (1892).
400. J. E. Drapeau to Glidden Co., U.S. pat. 2,115,063 (1938)—C.A. 32, 4766.
401. Eugen Dreher and Robert Otto, *Ann.*, 154, 178–82 (1870).
402. H. E. Drennan to Phillips Petroleum Co., (a) U.S. pat. 2,300,877 (1942); (b) 2,408,920 (1946); 2,422,826 (1947); (c) 2,452,040 (1948)—C.A. 37, 2554; 41, 772, 6274; 43, 2423.
403. A. M. Drummond and D. T. Gibson, *J. Chem. Soc.*, 1926, 3073–7—C.A. 21, 908.
404. C. P. Dubbs to U. O. Prods. Co., U.S. pat. 1,787,570 (1931)—C.A. 25, 808.
405. J. A. Dubbs, (a) U.S. pat. 407,182 (1889); (b) 470,911 (1892).
406. P. F. D. Dubois, *Fr. pat.* 757,379 (1933)—C.A. 28, 2880.
407. René Dubrisay, *Ann. combustibles liquides*, 8, 871–4 (1933)—C.A. 28, 621.
408. J. V. Dubsy, A. Okac, B. Okac, and J. Tritilek, *Chem Obzor*, 9, 173–4, 189–91 (*Eng.* 191) (1934)—C.A. 29, 2875.
409. A. M. Duckham and J. S. Morgan, U.S. pat. 1,527,847 (1925); 1,568,886 (1926)—C.A. 19, 1357; 20, 659.
410. A. P. Dumesny, *Fr. pat.* 845,453 (1939)—C.A. 35, 1062.
411. W. E. Duncan and Emil Ott, *J. Am. Chem. Soc.*, 53, 3940–9 (1931); 54, 4463 (1932)—C.A. 26, 390; 27, 35.
412. W. E. Duncan, Emil Ott, and E. E. Reid, *Ind. Eng. Chem.*, 23, 381–4 (1931)—C.A. 25, 2381.
413. H. V. Dunham, U.S. pat. 1,324,649 (1919)—C.A. 14, 470.
414. R. A. Dunham, U.S. pat. 1,982,577 (1934)—C.A. 29, 595.
415. C. L. Dunn to Shell Dev. Co., U.S. pat. 2,285,696 (1940)—C.A. 36, 7295.
416. A. E. Dunstan, *J. Soc. Chem. Ind.*, 39, 290A; *Petroleum Times*, 11, 63–5 (1924); *J. Inst. Pet. Tech.*, 10, 51–82, 201–5 (1924); *Chem. Weekbld.*, 21, 193–9 (1924); *Mon. petrole Roumain*, 25, 29–33 (1925)—C.A. 18, 749, 1563, 2072; 19, 1343.
417. A. E. Dunstan, (a) *Oil Gas J.*, 27, No. 30, 138–9 (1928); (b) *ibid.*, No. 42, 169, 175 (1929); (c) *Fuel Sci. Pract.*, 8, 441–456 (1931)—C.A. 23, 1742, 3335, 5563.

418. A. E. Dunstan, Austrian pat. 87,805 (1922); Brit. pat. 139,233 (1918); 184,281 (1921); 201,233, 204,078 (1922); U.S. pat. 1,435,824 (1922); 1,492,969 (1924); 1,549,469, 1,552,830 (1925)—C. 1922, IV, 909; C.A. 14, 2079; 17, 206; 18, 325, 899; 17, 467; 18, 2072; 19, 3013, 3586.
419. A. E. Dunstan, Brit. pat. 119,751 (1917); 204,078 (1922)—C.A. 13, 259; 18, 899.
420. A. E. Dunstan to Anglo Iranian Oil Co., Ltd., U.S. pat. 1,999,041 (1935)—C.A. 29, 4164.
421. A. E. Dunstan and B. T. Brooks, Oil Gas J., 21, No. 16, 14 (1922); Petr. Times, 8, 424 (1922); Petr. World, 19, 428 (1922); Ind. Eng. Chem., 14, 1112-5 (1922)—C.A. 17, 205.
422. A. E. Dunstan and F. B. Meadhurst, Brit. pat. 186,955 (1921)—C.A. 17, 1137.
423. A. E. Dunstan and F. G. P. Remfry, Brit. pat. 190,553 (1921)—C.A. 17, 2955.
424. A. E. Dunstan and F. B. Thole, Oil Gas J., 28, No. 1, 190, 194-5 (1929)—C.A. 23, 4054.
425. A. E. Dunstan and F. B. Thole, U.S. pat. 1,457,656 (1923)—C.A. 17, 2499.
426. A. E. Dunstan, F. B. Thole, and F. G. P. Remfry, J. Soc. Chem. Ind., 43, 179-88T (1924)—C.A. 18, 2802.
427. F. I. Du Pont, U.S. pat. 1,609,349 (1926)—C.A. 21, 317.
428. E. I. du Pont de Nemours & Co., (a) Brit. pat. 424,572 (1935); (b) 473,292 (1937); (c) Fr. pat. 821,580 (1937)—C.A. 29, 5216; 32, 3061, 3766.
429. C. G. Dyer and Charles Wirth, III, to U. O. Prods. Co., U.S. pat. 2,297,751 (1942)—C.A. 37, 1859.
430. LeRoy Eabey, Oil Gas J., 40, No. 37, 25-7 (1942)—C.A. 36, 4699; 37, 5228.
431. R. L. Eager and C. A. Winkler, Can. J. Research, 26B, 527-40 (1948)—C.A. 43, 120.
432. DuBois Eastman to The Texas Co., U.S. pat. 2,395,806 (1946)—C.A. 40, 2619.
433. L. T. Eby to S. O. Dev. Co., U.S. pat. 2,382,700 (1945)—C.A. 40, 723.
434. O. Eckart, Seifensieder-Ztg., 54, 82-3 (1927).
435. Lazar Edeleanu, U.S. pat. 911,553 (1909); Brit. pat. 11,140 of 1908—C.A. 3, 1082, 1213.
436. Lazar Edeleanu to Edeleanu-G. m. b. H., U.S. pat. 1,776,752 (1930)—C.A. 24, 5475.
- 436.5. Lazar Edeleanu and W. Hess, U.S. pat. 1,526,665 (1925)—C.A. 19, 1345.

437. Edeleanu-G. m. b. H., Ger. pat. 670, 596 (1939)—C.A. 33, 6581.
- 437.5. Harold Edelhoeh, Ephraim Katchalski, R. H. Maybury, W. L. Hughes, Jr., and J. T. Edsall, J. Am. Chem. Soc., 75, 5058–72 (1953)—C.A. 48, 1124.
438. E. A. Edwards, U.S. pat. 439,745 (1890).
439. J. E. Eggleston to S. O. Co., U.S. pat. 908,400 (1908); 1,018,040 (1912)—C.A. 6, 930.
440. Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,703,616 (1929); (b) 1,954,867 (1934); 2,291,886 (1942); (c) 1,960,624 (1934); (d) 1,962,182 (1934); (e) 2,009,879 (1935)—C.A. 23, 2030; 28, 3886; 37, 1259; 28, 4589, 4897; 29, 6414.
441. Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,575,905 (1926); (b) 1,803,964 (1931); (c) 2,325,115 (1943)—C.A. 20, 1514; 25, 3822; 38, 642.
442. Gustav Egloff and H. P. Benner, (a) U.S. pat. 1,535,653 (1925); (b) 1,569,855 (1926); (c) 1,608,089 (1926)—C.A. 19, 1944; 20, 817; 21, 318.
443. Gustav Egloff and C. D. Lowry, Jr., Ind. Eng. Chem., 20, 839–43 (1928)—C.A. 22, 3520.
444. Gustav Egloff, C. D. Lowry, Jr., and Paul Truesdell, Natl. Petroleum News, 22, No. 24, 41–3; No. 25, 69–72; No. 26, 79–80 (1930); Petroleum Z., 26, 919–27 (1930)—C.A. 24, 5473.
445. Gustav Egloff and J. C. Morrell, (a) Chem. Met. Eng., 28, 633–5 (1923); (b) Oil Age, 20, No. 5, 27–8 (1923); (c) Oil Gas J., 25, No. 39, 140–1 (1927)—C.A. 17, 2046; 18, 324; 21, 1543.
446. Gustav Egloff and J. C. Morrell, (a) Refiner Natural Gasoline Mfr., 2, No. 7, 5–7, 11–8 (1923); (b) Petroleum Times, 17, 777–8 (1927); (c) Petroleum, 24, 303–7 (1928).
447. Gustav Egloff and J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,733,656 (1929); (b) 2,040,366 (1936); (c) 2,057,424 (1936); (d) 2,063,494 (1936)—C.A. 24, 495; 30, 4660, 8596; 31, 846.
448. Gustav Egloff and J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,725,068 (1929); (b) 1,969,302 (1934); (c) 1,988,114 (1935); (d) 1,997,861 (1935)—C.A. 23, 4814; 28, 6295; 29, 1618, 3818.
449. Gustav Egloff, J. C. Morrell, W. L. Benedict, and Charles Wirth, III, Ind. Eng. Chem., 27, 323–9 (1935)—C.A. 29, 2716.

450. E. von Eichwald, Ger. pat. 399,628; U.S. pat. 1,550,523 (1925)—C.A. 20, 108.
451. A. S. Eigenson and E. P. Toporova, *Neftyanoe Khoz.*, 26, No. 2, 47-9 (1948)—C.A. 42, 7514.
452. J. C. Elgin, *Ind. Eng. Chem.*, 22, 1290-3 (1930)—C.A. 25, 1663.
453. J. C. Elgin, G. H. Wilder, and H. S. Taylor, *Ind. Eng. Chem.*, 22, 1284-90 (1930)—C.A. 25, 1663.
454. L. P. Elliott and M. H. Holm to Calif. Research Corp., U.S. pat. 2,440,258 (1948)—C.A. 42, 8456.
455. Carleton Ellis and J. V. Meigs, *Gasoline and Other Motor Fuels*, D. Van Nostrand Co., New York, 1921
456. Carleton Ellis, T. C. Whitner, and W. V. Keegan to S. O. Dev. Co., U.S. pat. 2,255,417 (1941)—C.A. 36, 648.
- 456.5. E. W. Ellis and Thomas Barker, *Anal. Chem.*, 23, 1777-9 (1951)—C.A. 46, 2964.
457. J. Ellis and E. C. Kattell, U.S. pat. 63,789 (1867).
458. L. M. Ellis, Jr., and E. E. Reid, (a) *J. Am. Chem. Soc.*, 54, 1674-87 (1932); (b) Read before the Petroleum Division A. C. S. Kansas City, April 1936—C.A. 26, 2697.
459. P. W. Emery, *Natl. Petr. News*, 32, No. 34, R 302-3 (1940).
460. A. F. Endres to S. O. of Ind., U.S. pat. 1,996,236, 2,022,847 (1935)—C.A. 29, 3509; 30, 851.
461. W. F. Engel to N. V. de Bataafsche, Dutch pat. 61,745 (1948)—C.A. 43, 390.
462. E. F. Engelke, U.S. pat. 1,986,565 (1935)—C.A. 29, 1238.
463. C. Engler, *Dingler's Poly. J.*, 250, 316-321 (1883).
464. C. Engler and H. Broniatowski, *Ber.*, 37, 3274-6 (1904).
465. C. Engler and L. Ubbelohde, *Z. angew. Chem.*, 26, 177-78 (1913)—C.A. 7, 2299.
466. B. A. Englin, *Neftyanoe Khoz.*, 1939, No. 8, 36-40—C.A. 34, 3483.
467. B. A. Englin and V. T. Brazhnikov, *Novosti Tekniki*, 1939, No. 35-6, 26-7; *Vostochnaya Neft*, 1939, No. 4-5, 49-55; *Khim. Referat. Zhur.*, 1940, No. 6, 110—C.A. 34, 4893; 36, 5339.
468. O. L. Erdmann, *J. prakt. Chem.*, 34, 447 (1845).
469. Erdöl- u. Kohle-Verwertung A.-G., Ger. pat. 469,228 (1928)—C. 1929, I. 2850.
470. C. Erkstrand, U.S. pat. 1,388,415 (1921)—C.A. 15, 4048.
471. Emil Erlenmeyer, *Zeit. f. Chemie*, 1861, 660.
472. Emil Erlenmeyer and Lisenko, *Jahresb.*, 1861, 590.

473. Emil Erlenmeyer and J. A. Wanklyn, *Ann.*, **135**, 129–51 (1865).
474. J. C. Ernest to Mid-West Refineries, Inc., U.S. pat. 2,421,320 (1947)—*C.A.* **41**, 7104.
475. Ferd Escherich, Bruno Pretzsch and Otto Danguillier, *Ger. pat.* 392,206 (1924)—*C.* **1924**, I, 2655.
476. R. H. Espach and O. C. Blade, *Bur. Mines, Tech. Paper*, **513**, 22 p. (1931)—*C.A.* **26**, 1106.
477. E. V. Evans, U.S. pat. 1,257,829 (1918)—*C.A.* **12**, 994.
478. E. V. Evans and So. Metropolitan Gas Co., *Brit. pat.* 22,147 of 1914; *Fr. pat.* 480,129 (1916)—*C. A.* **10**, 1266; **11**, 1296.
479. O. B. Evans, *Gas Record*, **15**, 215–6 (1919); *Gas Age*, **43**, 475–6 (1919)—*C.A.* **13**, 1380.
480. R. L. Evans and E. G. McDonough, *Brit. pat.* 521,240 (1940)—*C.A.* **36**, 1144.
481. T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, **52**, 3645–7 (1930)—*C.A.* **24**, 5028.
482. B. L. Evering, A. P. Lien, and J. M. Page, Jr., to S. O. Co. of Ind., U.S. pat. 2,450,588 (1948)—*C.A.* **44**, 2228.
483. W. L. Evers to Socony-Vac. Oil Co., U.S. pat. 2,088,193 (1937)—*C.A.* **31**, 6867.
484. L. M. Fanning, *Oil Gas J.*, **24**, No. 19, 352 (1925).
485. W. F. Faragher, J. C. Morrell, and S. Comay, *Ind. Eng. Chem.*, **20**, 527–32 (1928)—*C.A.* **22**, 2459.
486. W. F. Faragher, J. C. Morrell, and G. S. Monroe, (a) *Ind. Eng. Chem.*, **19**, 1281–4 (1927); (b) *ibid.*, 1647—*C.A.* **22**, 2266.
487. M. W. Farlow, Madison Hunt, C. M. Langkammerer, W. A. Lazier, W. J. Peppel, and F. K. Signaigo, *J. Am. Chem. Soc.*, **70**, 1392–4 (1948)—*C.A.* **42**, 5420.
488. E. H. Farmer and F. W. Shipley, *J. Chem. Soc.*, **1947**, 1519–32—*C.A.* **43**, 995.
489. A. Farrar, (a) U.S. pat. 96,097 (1869); (b) 100,876 (1870); (c) 129,014 (1872).
490. Heinrich Fasbender, *Ber.*, **21**, 1470–2 (1888).
491. H. W. Faucett and T. McGowan, U.S. pat. 133,425 (1872).
492. C. B. Faught, (a) *Refiner Natural Gasoline Mfr.*, **10**, No. 4, 179; No. 5, 70 (1931); (b) *ibid.*, **11**, No. 4, 272 (1932)—*C.A.* **25**, 4112; **26**, 3097.
493. E. W. M. Fawcett and E. S. Narracott to Anglo-Iranian Oil Co., U.S. pat. 2,389,659 (1945)—*C.A.* **40**, 1531.
- 493.5. C. F. Feasley to Socony-Vac. Oil Co., U.S. pat. 2,502,001 (1950)—*C.A.* **44**, 6617.

494. Fritz Feigl, *Mikrochemie*, 15, 1-8 (1934)—C.A. 28, 6393.
495. Fritz Feigl and G. F. Dacorso, Ministério agr., Dept. nacl. produçao mineral., Lab. produçao mineral. (Brazil), Bol. No. 5, 147-58 (1942)—C.A. 38, 2585.
- 495.5. Benjamin Feiner, W. J. Burke, and Samuel Moskowitz, *J. Ind. Hyg. Toxicol.*, 28, 276-7 (1946)—C.A. 41, 1577.
496. E. Ferber, *Z. angew. Chem.*, 41, 680-2 (1928)—C.A. 22, 4237.
497. L. C. Fetterly to Shell Dev. Co., U.S. pat. 2,426,087, 2,432,301 (1947); 2,451,817 (1948); 2,472,473 (1949); 2,557,643 (1951)—C.A. 41, 7100; 43, 1793, 7223; 45, 8214.
498. H. W. Field, *Natl. Pet. News*, 33, No. 40, R316-8 (1941); *Refiner Nat. Gasoline Mfr.*, 20, 419-21 (1941); *Oil Gas J.*, 40, No. 20, 40, 41 (1941)—C.A. 36, 1474, 4699.
499. J. D. Fields, (a) U.S. pat. 1,864,687 (1932); 1,864,719 (1932); 1,983,220 (1934); 2,027,770 (1936); (b) 2,024,968 (1935)—C.A. 26, 4464; 29, 589; 30, 1554, 1224.
500. J. Fielschmidt and T. L. Cantrell, *Refiner*, 9, No. 2, 97 (1930)—C.A. 24, 5145.
501. J. G. Fife, (a) Brit. pat. 527,509 (1940); (b) 563,930 (1944)—C.A. 35, 7073; 40, 2972.
502. Franz Fischer and H. Tropsch, Brit. pat. 254,288 (1925)—C.A. 21, 2552.
503. H. G. M. Fischer to S. O. Dev. Co., (a) Brit. pat. 295,728 (1927); U.S. pat. 1,767,356 (1930); 2,369,554 (1945); (b) 1,970,693 (1934); 2,338,579 (1944); (c) 1,795,278 (1931); (d) 2,001,715 (1935)—C.A. 23, 2291; 24, 4384; 39, 4468; 28, 6296; 38, 4430; 25, 2278; 29, 4379.
504. H. G. M. Fischer and W. J. Addems, Brit. pat. 270,626 (1925); Can. pat. 278,206 (1928); U.S. pat. 1,789,335 (1931)—C.A. 22, 1676, 2835; 25, 1373.
505. W. M. Fitzhugh, Jr., *Laryngoscope*, 48, 884-903 (1938)—C.A. 33, 2214.
506. Ogden FitzSimons and W. H. Bahlke to S. O. Co. of Ind., Can. pat. 357,077 (1936); U.S. pat. 2,073,517 (1937)—C.A. 30, 4001; 31, 3683.
507. Ogden FitzSimons and F. C. Croxton to S. O. Co. of Ind., U.S. pat. 2,063,597 (1936)—C.A. 31, 851.
508. B. Flaschenträger and G. Wannschaff, *Ber.*, 67, 1121-4 (1934)—C.A. 28, 5401.
509. Richard Fleming to Richard Fleming Co., U.S. pat. 1,325,668 (1919); Brit. pat. 135,855 (1919)—C.A. 14, 466, 1217.

510. W. E. Fleming and F. E. Baker, U.S. Bur. Ent. & Plant Quar. News Letter, 2, (11) 7 (1935).
511. G. W. Flowers, J. C. Happersett, and D. W. Happersett, U.S. pat. 74,756 (1868).
512. Abraham Fookson and A. D. Bell, Petroleum Refiner, 27, No. 9, 459-67 (1948)—C.A. 43, 384.
513. L. A. Ford and D. F. Clausen, Ind. Eng. Chem., News Ed., 19, 783 (1941)—C.A. 35, 6016.
514. Dan Fore, Jr., and R. W. Bost, J. Am. Chem. Soc., 59, 2557-8 (1937)—C.A. 32, 911.
515. G. F. Forwood and J. G. Taplay, Brit. pat. 129,349 (1917)—C.A. 13, 3007.
516. A. L. Foster (a) Petroleum Engr., 11, No. 9, 49-52 (1940); (b) Oil Gas J., 42, No. 7, 111, 112, 115, 116 (1943); (c) *ibid.*, 38, No. 19, 67 (1939); *ibid.*, 46, No. 31, 74-6, 111-3 (1947); Natl. Petr. News, 31, No. 38, 394-403 (1939); Refiner Natural Gasoline Mfr., 18, No. 10, 80-6 (1939)—C.A. 34, 7096; 37, 6859; 42, 2751.
517. M. J. Fowle and R. D. Bent, Oil Gas J., 46, No. 28, 209-15; Petroleum Processing, 2, No. 12, 935-42 (1947); Petroleum Refiner, 26, No. 11, 87 (719)-95 (727)—C.A. 42, 1725.
518. M. J. Fowle and H. W. Field, World Petroleum, 13, No. 2, 44-7 (1942)—C.A. 36, 5637.
519. A. L. Fox to Du Pont Co., U.S. pat. 2,349,820 (1944); 2,414,035 (1947); Brit. pat. 580,366 (1946)—C.A. 39, 1534; 41, 2237, 1710.
520. Francis Francis, Ber., 39, 3803 (1906)—C.A. 1, 424.
521. R. L. Frank, P. V. Smith, F. N. Woodward, W. B. Reynolds, and P. J. Canterino, J. Polymer Sci., 3, 39-49 (1948)—C.A. 42, 3986.
522. Adolf Franke and Rudolf Dworzak, Monatsh., 43, 661-71 (1923)—C.A. 17, 2103.
523. C. J. Frankforter to Frankforter Oil Process Inc., U.S. pat. 1,780,873 (1930); Reissue 18,318 (1931); Fr. pat. 703,226 (1930)—C.A. 25, 200; 26, 1432; 25, 4394.
524. L. U. Franklin to Gulf Oil Corp., U.S. pat. 2,235,921 (1941); 2,284,273 (1942)—C.A. 35, 4587; 36, 7294.
525. L. U. Franklin and W. H. Weeks to Gulf Oil Corp., U.S. pat. 2,284,271 (1942)—C.A. 36, 7294.
526. L. U. Franklin, W. H. Weeks, and J. W. Harris to Gulf Oil Corp., U.S. pat. 2,284,272 (1942)—C.A. 36, 7294.
527. Herman Frasch, Ind. Eng. Chem., 4, 134-40 (1912)—C.A. 6, 796.

528. Herman Frasch, (a) U.S. pat. 378,246 (1888); (b) 487,216 (1892); (c) 525,811 (1894); (d) 542,849 (1895); (e) 622,799, 630,496 (1899); 649,047, 649,048 (1900).
529. Herman Frasch, (a) U.S. pat. 448,480 (1891); 490,114, 500,252 (1893); (b) 487,119 (1892); (c) 543,619 (1895); 564,920, 564,921, 564,922 (1896); (d) 561,216 (1896); (e) 564,923, 564,924 (1896).
530. Herman Frasch to S. Oil Co., U.S. pat. 951,272 (1910)—C.A. 4, 1542.
531. G. Free, Brennstoff Chem., 18, 25–31 (1937)—C.A. 31, 4800.
532. N. H. Freeman, Brit. pat. 193,979 (1921)—C.A. 17, 3603.
533. D. M. French, Paint, Oil, Chem. Rev., 112, No. 20, 15, 26, 28, 30, 32 (1949)—C.A. 44, 3267.
- 535.5. Hans Freytag, Z. anal. Chem., 138, 259–66 (1953)—C.A. 47, 7374.
534. L. H. Friedburg, U.S. pat. 306,734 (1884).
535. Charles Friedel and J. M. Crafts, (a) Chem. Ind., 1878, 411—Jahresber., 1878, 1166; Compt. rend., 84, 1392 (1878); (b) Brit. pat. 4,769 of 1877.
536. Charles Friedel and A. Ladenburg, Ann., 145, 189 (1868).
537. Walter Friedmann, Erdöl u. Teer, 6, 285–6, 301–3, 342–4, 359–63 (1930); Oil Gas J., 29, No. 31, 32, 106, 107 (1930)—C.A. 24, 5989; 25, 1981.
538. Walter Friedmann and Carlos Rodriguez, Petroleum Refiner, 25, No. 2, 53–60 (1946)—C.A. 40, 2285.
539. I. T. Fritz, Oil Gas J., 48, No. 42, 180 (1950)—C.A. 44, 4663.
540. P. K. Frolich to S. O. Dev. Co., U.S. pat. 2,035,121 (1936)—C.A. 30, 2985.
541. P. K. Frolich and P. J. Wiezevich to S. O. Dev. Co., U.S. pat. 2,045,766 (1936)—C.A. 30, 5596.
542. B. A. Frolov to Shell Dev. Co., (a) U.S. pat. 2,213,801 (1940); (b) Can. pat. 426,405 (1945)—C.A. 35, 888; 39, 2643.
543. Emil Fromm and Carltheo Shultis, Ber., 56, 937–47 (1923)—C.A. 17, 3014.
544. W. C. Fry and B. F. Hartman to Socony-Vac. Oil Co., U.S. pat. 2,297,650 (1942)—C.A. 37, 1860.
545. C. F. Fryling to B. F. Goodrich Co., U.S. pat. 2,401,346 (1946)—C.A. 40, 4907.
546. A. Fürth and M. Jaenicke, Z. angew. Chem., 38, 166–73 (1925)—C.A. 19, 1486.

547. Wataru Funasaka, *Sci. Papers Inst. Chem. Phys. Research*, **37**, 323–30, 331–7 (1940)—*C. 1940*, II, 2842.
- 547.5. Wataru Funasaka, Ryokichi Fukushima, Tomio Jinta, Tesuo Inaba, Itsuo Matsubara, and Masayasu Yuguchi, *J. Soc. Chem. Ind. Japan*, **50**, 125–6 (1947)—*C.A.* **44**, 9136.
548. F. D. Fuqua, *Petroleum Processing*, **3**, 1050–1 (1948)—*C.A.* **43**, 2761.
549. S. Gabriel and J. Colman, *Ber.*, **45**, 1643–54 (1912)—*C.A.* **6**, 2618.
550. S. Gabriel and A. Deutsch, *Ber.*, **13**, 386–91 (1880).
551. S. M. Gabriel'yantz and O. A. Artem'eva, *Groznenskii Neftyanik*, **4**, No. 8, 41–5 (1934)—*C.A.* **29**, 2725.
552. R. Gaggin, (a) U.S. pat. 118,359 (1871); (b) 138,629 (1873).
553. Ernst Galle and Walter Michelitsch, *Montan. Rundschau*, **27**, No. 5, 1–8 (1935); *Petroleum*, **31**, No. 8, 1–8 (1935)—*C.A.* **29**, 4251, 7060.
554. Frank Gardner, U.S. pat. 2,073,147, 2,082,331 (1937)—*C.A.* **31**, 3253, 5560.
555. F. T. Gardner, *Chem. Met. Eng.*, **39**, 378–9 (1932)—*C.A.* **26**, 5408.
556. F. T. Gardner and E. C. Higgins, Jr., *Ind. Eng. Chem.*, **24**, 1141–6 (1932)—*C.A.* **26**, 6106–7.
557. J. Gardner and J. F. Harris, U.S. pat. 442,802 (1890).
558. J. A. Gardner to Monsanto Chemicals Ltd., (a) U.S. pat. 2,385,410 (1945); (b) Brit. pat. 574,773 (1946)—*C.A.* **40**, 21; **43**, 1067.
559. J. A. Gardner and Monsanto Chemicals Ltd., Brit. pat. 572,669 (1945)—*C.A.* **43**, 7036.
560. R. H. Gardner and H. G. Hodge to Sinclair Refg. Co., U.S. pat. 1,740,584 (1929)—*C.A.* **24**, 1211.
561. W. W. Gary, *Petroleum World & Oil Age*, **26**, No. 12, 67–70 (1929)—*C.A.* **24**, 1208.
562. W. W. Gary, U.S. pat. 1,677,440 (1928); 1,893,138, 1,929,489 (1933); 1,994,511 (1935); 2,041,754 (1936)—*C.A.* **22**, 3289; **27**, 2291; **28**, 307; **29**, 3146; **30**, 5024.
563. W. W. Gary, one half to C. O. Middleton, U.S. pat. 1,893,138 (1933)—*C.A.* **27**, 2291.
564. Gas Research Board and Arthur Key, Brit. pat. 561,679, 563,350 (1944)—*C.A.* **40**, 197, 2285.
565. Wilhelm Gaus and Mathias Pier to I. G. Farben., U.S. pat. 1,932,174 (1933)—*C.A.* **28**, 624.

566. Martin Geissler, *Braunkohlenarch.*, No. 43, 1-10 (1935)—C.A. 30, 3992.
567. M. H. Gerasimov and V. E. Glushnev, *Neftyanoe Khoz.*, 1949, No. 1, 22-5.
568. M. M. Gerasimov, V. E. Glushnev, S. N. Solodov, A. N. Tsyba, and M. N. Sharonov, *Neftyanoe Khoz.*, 1939, No. 6, 43-5—C.A. 34, 8239.
569. M. M. Gerasimov, V. E. Glushnev, S. F. Vasil'ev, and S. N. Solodov, *Neftyanoe Khoz.*, 1940, No. 2, 23-6—C.A. 34, 8239.
570. E. Gerathewohl, *Ann.*, 56, 303-5 (1845).
- 570.5. M. I. Gerber, *Zhur. Anal. Khim.*, 2, 265-73 (1947)—C.A. 43, 6943.
571. W. A. Gersdorff, *Protoplasma*, 31, 199-206 (1938)—C.A. 33, 3004.
572. D. F. Gerstenberger, *Natl. Petroleum News*, 21, No. 8, 61, 64, 66 (1929)—C.A. 23, 3335.
573. Gevaert Photo-Producten, N. V., Belg. pat. 437,217 (1939)—C.A. 36, 2486.
574. Gewerkschaft Mathias Stinnes, Brit. pat. 425,938 (1935)—C.A. 29, 6417.
575. R. L. Gholson, U.S. pat. 2,303,835 (1942)—C.A. 37, 3263.
576. G. R. Gilbert to S. O. Dev. Co., (a) U.S. pat. 2,334,549 (1943); (b) 2,369,558 (1945)—C.A. 38, 3813; 39, 4470.
577. C. E. Gill, *Gas*, 15, No. 6, 24, 29 (1939)—C.A. 33, 6028.
578. Henry Gilman and J. F. Nelson, *J. Am. Chem. Soc.*, 59, 935-7 (1937)—C.A. 31, 4265.
579. Henry Gilman, Mary A. Plunkett, L. Tolman, L. Fullhart, and H. S. Broadbent, *J. Am. Chem. Soc.*, 67, 1845-6 (1945)—C.A. 40, 60.
580. Henry Gilman and H. L. Yale, *J. Am. Chem. Soc.*, 73, 2880-1, 4470-1 (1951)—C.A. 46, 3974.
581. J. E. Gilpin and O. E. Bransky, *U.S. Geol. Survey, Bull.*, 475, 50 p.; *Am. Chem. J.*, 44, 251 (1910)—C.A. 5, 375.
582. J. E. Gilpin and P. Schneeberger, *Am. Chem. J.*, 50, 59-100 (1913)—C.A. 7, 3408.
583. L. G. Gindin, I. I. Torsuev, and V. A. Kazakova, *Compt. rend. acad. Sci.*, (USSR), 16, 413-8 (1937)—C.A. 32, 3313.
584. I. Ginsberg, *Refiner Natural Gasoline Mfr.*, 4, No. 11, 16 (1925)—C.A. 20, 1319.
585. J. M. Ginsburg and C. J. Cavallito, *J. Econ. Entomol.*, 29, 856-9 (1936)—C.A. 31, 1149.

586. V. E. Glushnev and M. M. Gerasimov, *Vostochnaya Neft*, 1940, No. 12, 29–30; *Khim. Referat. Zhur.*, 4, No. 9, 120 (1941)—C.A. 38, 1867.
587. V. E. Glushnev and S. F. Vasil'ev, *Izvest. Akad. Nauk SSSR Otdel. Tekh. Nauk*, 1947, 829–33—C.A. 43, 8125.
588. C. Godard, *Brit. pat.* 22,085 of 1903.
589. J. Gössl and R. O. Herzog, *Z. physiol. Chem.*, 88, 103–8 (1913)—C.A. 8, 1293.
590. H. P. J. B. Goffart, *Fr. pat.* 350,091 (1904).
591. D. L. Gol'dshtein and A. Ya. Semenova, *Vostochnaya Neft*, 1939, No. 2, 22–4 Translation: *Foreign Petroleum Tech.*, 8, 285–91 (1940)—C.A. 34, 8238.
592. H. Goldwater, *U.S. pat.* 432,525 (1890).
593. R. E. Goode, (a) *Refiner*, 8, No. 7, 77–80 (1929); (b) *Oil Gas J.*, 28, No. 23, 46, 148 (1930)—C.A. 23, 4562; 24, 2871.
594. T. J. Gordon, *U.S. pat.* 451,724 (1891).
595. George Gorin, Gregg Dougherty, and A. V. Tobolsky, *J. Am. Chem. Soc.*, 71, 3551 (1949)—C.A. 44, 1008.
596. N. Grabowsky and Alexander Saytzeff, *Ann.*, 171, 251–8 (1874).
597. A. J. Gracia to Wingfoot Corp., *U.S. pat.* 2,119,131 (1938)—C.A. 32, 5413.
598. Edward Graefe, *Petroleum Z.*, 1, 606 (1905–06); *Gas World*, 58, 752 (1913)—C.A. 7, 2851.
599. J. B. Grant and A. Mason, *U.S. pat.* 339,546 (1886).
600. Grasselli Chem. Co., *Brit. pat.* 436,327 (1935)—C.A. 30, 1936.
601. R. J. Gaul and J. V. Karabinas, *Science*, 104, 557 (1946)—C.A. 41, 2397.
602. F. G. Graves, *Ind. Eng. Chem.*, 31, 850–6 (1939)—C.A. 33, 6577.
603. F. G. Graves, *U.S. pat.* 1,867,697 (1932)—C.A. 26, 5200.
604. J. L. Gray, *U.S. pat.* 1,474,147 (1923)—C.A. 18, 465.
605. L. R. Gray, *Petroleum Refiner*, 23, 388–94 (1944); *Petroleum Engr.*, 16, No. 1, 160–78 (1944)—C.A. 39, 405; 40, 3590.
606. T. H. Gray, *Brit. pat.* 5,132 of 1889—*J. Soc. Chem. Ind.*, 8, 467 (1889).
607. T. T. Gray, *U.S. pat.* 1,340,889 (1920)—C.A. 14, 2261.
608. T. T. Gray to Gray Processes Corp., (a) *U.S. pat.* 1,768,683 (1930); (b) 1,825,861 (1931); (c) 1,937,113 (1933); 1,952,751 (1934); (d) 2,019,184 (1935)—C.A. 24, 4624; 26, 589; 28, 1179, 3576; 30, 281.

609. T. T. Gray and M. R. Mandelbaum, *Ind. Eng. Chem.*, **16**, 913-6 (1924)—C.A. **18**, 3473.
610. B. A. Greensfelder and M. E. Spaght to Shell Dev. Co., U.S. pat. 2,174,174 (1939)—C.A. **34**, 615.
611. C. J. Greenstreet, U.S. pat. 1,110,925 (1914)—C.A. **8**, 3628.
612. E. Juanita Greer, *Ind. Eng. Chem.*, **21**, 1033 (1929)—C.A. **24**, 493.
- 612.5. D. C. Gregg, H. A. Iddles, and P. W. Stearns, Jr., *J. Org. Chem.*, **16**, 246-52 (1951)—C.A. **45**, 8485.
613. R. A. Gregg, D. M. Alderman, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3740-3 (1948)—C.A. **43**, 1340.
614. Gregory, *Ann.*, **15**, 239-40 (1835).
615. L. S. Gregory to Phillips Petroleum Co., U.S. pat. 2,197,799 (1940)—C.A. **34**, 6061.
616. R. C. Griffin, *Analytical Chem.*, **1**, 167-9 (1929)—C.A. **23**, 4332.
617. R. H. Griffith, *Inst. Gas Engrs. Copyright Publication*, No. 175/64, 45-64; *Gas J.*, **220**, 475-6, 479-85, 667; *Gas World*, **107**, 379-83, 471-6, 563—C.A. **32**, 6438.
618. R. H. Griffith and S. G. Hill, *J. Chem. Soc.*, **1938**, 717—C.A. **32**, 6138.
619. R. H. Griffith and J. H. G. Plant, *Gas J.*, **244**, 48-50, 53-4 (1944); *Gas World*, **121**, 28-36 (1944)—C.A. **38**, 5063, 5661.
620. R. H. Griffith and J. H. G. Plant to The Gas Light and Coke Co., U.S. pat. 2,193,278 (1940); 2,295,653 (1942)—C.A. **34**, 4891; **37**, 1247.
621. G. F. Grillot and T. J. Brooks, Jr., *J. Am. Chem. Soc.*, **72**, 4281 (1950)—C.A. **45**, 2896.
622. G. F. Grillot, P. M. Levin, Richard Green, and R. I. Bashford, *J. Am. Chem. Soc.*, **72**, 1863 (1950)—C.A. **44**, 5838.
623. H. P. A. Groll and George Hearne to N. V. Bataafsche, *Brit. pat.* 449,783 (1936)—C.A. **30**, 8598.
624. H. H. Gross to The Texas Co., U.S. pat. 1,962,103 (1934)—C.A. **28**, 4897.
625. H. H. Gross, W. E. Skelton, and J. C. Best, *Oil Gas J.*, Mar. **23**, 1950, 211-3, 332.
626. A. V. Grosse to U. O. Prods. Co., U.S. pat. 2,029,100, 2,037,781 (1936)—C.A. **30**, 1987, 4000.
627. I. W. Grote, *J. Biol. Chem.*, **93**, 25-30 (1931)—C.A. **25**, 5876.

628. A. Guiselin, (a) *Petroleum*, 6, 133—2nd Int. Cold Congress; (b) *J. Inst. Petroleum Tech.*, 10, 918–46 (1924); *Chimie et industrie*, 12, 423–40 (1924)—C.A. 5, 376; 19, 394.
629. Leo Gurwitsch, *Wissenschaftliche Grundlagen der Erdölverarbeitung*, 2nd Edition, 1924, Berlin, Julius Springer.
630. Leo Gurwitsch and A. Moore, *Scientific Principles of Petroleum Technology*, New York, D. Van Nostrand Co., Inc., 1934.
631. S. L. Gusinskaya, *Acta Univ. Asiae Mediae*, Ser. VI, *Chemia*, No. 42, 6 p. (1938)—C.A. 34, 3482.
632. G. Gustavson, *Ber.*, 14, 2619–23 (1881); *J. Russ. Phys. Chem. Soc.*, 13, 149 (1880)—C. 1881, 353.
633. F. W. Guthke to I. G. Farben., U.S. pat. 1,897,798 (1933)—C.A. 27, 2691.
634. Boyd Guthrie and M. C. Simmons, U.S. Bur. Mines Rept. Invest., 3729, 16 p. (1943)—C.A. 41, 5290.
635. J. D. Guthrie, *Contribn. Boyce Thompson Inst.*, 12, 45–7 (1941)—C.A. 35, 4906.
636. V. B. Guthrie, (a) *Natl. Petroleum News*, 14, No. 7, 34, 37–8 (1922); (b) *ibid.*, 18, No. 29, 17–8 (1926)—C.A. 16, 1312; 20, 3559.
637. H. C. Guy, *Del. Agr. Expt. Sta. Bull.*, 206, (Tech. Bull. 19), 60 p. (1937)—C.A. 31, 6806.
638. J. A. Guyer to Phillips Petroleum Co., U.S. pat. 2,338,581 (1944)—C.A. 38, 4430.
639. M. H. Gwynn, U.S. pat. 2,073,578 (1937)—C. A. 31, 3255.
640. J. E. Hackford, *J. Inst. Petr. Techn.*, 12, 135–6 (1926).
641. Vladimir Haensel, *Petroleum Processing*, 5, 356–60; *Petroleum Refiner*, 29, No. 4, 131–6; *Petroleum Engr.*, 22C, No. 4, 9–14 (1950); *Oil Gas J.*, 48, No. 47, 85; 82–85, 114, 119; *Calif. Oil World*, 43, No. 7, 3, 5, 7–9, 11, 13 (1950)—C.A. 44, 6610.
642. A. Hagemann and K. I. Skärblom, *Braunkohle*, 31, 152–7, 171–5 (1932)—C.A. 26, 2577.
643. W. E. Haines, W. J. Wenger, R. V. Helm, and J. S. Ball, U.S. Bur. Mines Rept. Investigations, 4060 (1946).
644. J. H. Hale, M. C. Simmons, and F. P. Whisenhunt, *Ind. Eng. Chem.*, 41, 2702–8 (1949)—C.A. 44, 2212.
645. J. H. Hale, C. J. Thompson, M. G. Barker, H. M. Smith, and J. C. Ball, A.C.S. Meeting, March 26–30, 1950, Houston, Tex.

646. F. W. Hall to The Texas Co., U.S. pat. 2,091,239 (1937)—C.A. 31, 7638.
647. F. W. Hall and C. E. Lauer to The Texas Co., U.S. pat. 1,936,086 (1933)—C.A. 28, 887.
648. T. G. Hall, U.S. pat. 372,672 (1897).
649. W. A. Hall, U.S. pat. 1,239,100 (1917)—C.A. 11, 3427.
650. H. J. Halle to U. O. Prods. Co., U.S. pat. 1,681,638 (1928)—C.A. 22, 3984.
651. Albin Haller and E. Michel, Bull. soc. chim., (3) 15, 1065-70 (1897).
652. Albin Haller, Paul Sabatier and J. B. Sanderens, Fr. pat. 376,490 (1906)—C.A. 3, 245.
653. R. L. Hallett to Natl. Lead Co., U.S. pat. 1,678,984 (1928)—C.A. 22, 3772.
654. R. L. Hallett and W. H. Sowers, Petroleum Engr., 1, No. 8, 78-81 (1930)—C.A. 24, 3892.
- 654.5. E. G. Hallonquist, Modern Plastics, 27, No. 12, 100, 152 (1950)—C.A. 44, 8157.
655. R. A. Halloran, Oil Gas J., 26, No. 29, 36, 147 (1927); Natl. Petroleum News, 25, No. 30, 35-6, 38, 40 (1933); World Petr. Cong., London, 1933, Proc. 2, 3-6—C.A. 22, 1465; 27, 5523.
656. R. A. Halloran, M. L. Chappell, and J. H. Osmer, U.S. pat. 1,872,446 (1932)—C.A. 26, 6116.
657. H. Halvorson, U.S. pat. 305,181 (1894).
658. J. H. Hamence, Analyst, 65, 152-4 (1940)—C.A. 34, 2729.
659. W. G. Hamilton, R. G. Follis, and H. P. McCormick, U.S. pat. 1,993,140 (1935)—C.A. 29, 2731.
660. F. S. Hammett, Protoplasma, 13, 331-47 (1931)—C.A. 26, 1349.
661. F. S. Hammett and S. S. Chapman, J. Lab. Clin. Med., 24, 293-8 (1938)—C.A. 33, 5018.
662. F. S. Hammett and D. W. Hammett, Protoplasma, 16, 253-86 (1932)—C.A. 27, 3009.
663. F. S. Hammett and S. P. Reimann, J. Exptl. Med., 50, 445-8 (1929)—C.A. 23, 5479.
664. F. S. Hammett and Dorothy W. Smith, Protoplasma, 13, 261-7 (1931)—C.A. 26, 1037.
665. F. S. Hammett and Louise P. Wilson, Growth, 7, 183-97 (1943)—C.A. 38, 416.

666. W. T. Hancock, U.S. pat. 2,097,097 (1937); 2,162,715 (1939); 2,225,172 (1940); 2,260,617, 2,260,618, 2,260,620 (1941); 2,288,131, 2,303,547 (1942); 2,308,172 (1943)—C.A. 32, 344; 33, 7999; 35, 2710; 36, 1481, 1173, 1478; 37, 524, 2920, 3923.
667. W. T. Hancock, to Hancock Oil Co. of Calif., U.S. pat. 2,316,954 (1943)—C.A. 37, 6120.
668. T. K. Hanson and K. F. Coles, J. Inst. Petroleum, 33, 589-97 (1947)—C.A. 42, 3164.
669. John Happel and S. P. Cauley, (a) Refiner Natural Gasoline Mfr., 19, No. 6, 89-92 (1940); (b) *ibid.*, 19, 205-8 (1940); Proc. Am. Petroleum Inst., 10th Mid-Year Meeting, Sect. III, 21, 96-104 (1940); (c) Ind. Eng. Chem., 39, 1655-9 (1947)—C.A. 34, 5638, 7095; 42, 1413.
670. John Happel, S. P. Cauley, and H. S. Kelly, Proc. Am. Petroleum Inst., 23, III. 67-77 (1942); Petroleum Refiner, 21, 406-13 (1942); Oil Gas J., 41, No. 27, 136, 139, 140, 142, 147, 148, 150, 152 (1942)—C.A. 37, 1250, 6863.
671. John Happel and D. W. Robertson, (a) Ind. Eng. Chem., 27, 941-3 (1935); (b) Oil Gas J., 36, No. 46, 125-6, 128 (1938)—C.A. 32, 8752.
672. John Happel, Jr., and D. W. Robertson to Socony-Vac. Oil Co., (a) U.S. pat. 2,102,796 (1937); (b) 2,273,263 (1942)—C.A. 32, 1439; 36, 4327.
673. Joseph Haraszti, J. prakt. Chem., [2] 149, 301-10 (1937)—C.A. 32, 528.
674. Dorothy Haresnape, F. A. Fidler, and R. A. Lowry, Ind. Eng. Chem., 41, 2691-7 (1949)—C.A. 44, 2214.
- 674.5. D. P. Harnish and D. A. Tarbell, Anal. Chem., 21, 968-9 (1949)—C.A. 43, 8978.
675. C. Harries, Ber., 52, 65-72 (1919)—C.A. 13, 1590.
676. C. Harries to Siemens and Halske, Ger. pat. 439,005 (1926)—C. 1927, I, 1256.
677. D. Harrington and J. H. East, Jr., U.S. Bur. Mines, Cir. 7246, 7 p. (1943)—C.A. 37, 6765.
678. P. J. Harrington to S. O. Dev. Co., U.S. pat. 2,293,205 (1942); 2,367,348 (1945)—C.A. 37, 1259; 39, 3923.
679. D. C. Harrison, Biochem. J., 21, 335-46 (1927)—C.A. 21, 2594.
680. W. W. Hartman, L. A. Smith, and J. B. Dickey, Ind. Eng. Chem., 24, 1317-18 (1932)—C.A. 27, 71.
- 680.5. Heinrich Hauptmann, Blanka Wladislaw, Lucy L. Nazario and W. F. Walter, Ann., 576, 45-60 (1952)—C.A. 47, 3814.

681. B. N. Hawes, U.S. pat. 444, 833 (1891).
682. L. F. Hawley, *Ind. Eng. Chem.*, 9, 866-71 (1917)—C.A. 11, 3098.
683. A. Hayes, U.S. pat. 1,428,885 (1922)—C.A. 16, 3751.
684. H. L. Hayes to Phillips Petroleum Co., U.S. pat. 2,378,079 (1945)—C.A. 39, 3658.
685. J. W. Healy and W. R. Hertwig, ACS Meeting, Sept. 18-23 (1949), Atlantic City.
686. R. Heap and B. C. Saunders, *J. Chem. Soc.*, 1949, 2983-8—C.A. 44, 3880.
687. F. W. Heath to Shell Dev. Co., Can. pat. 327,496 (1932); U.S. pat. 1,888,382 (1932)—C.A. 27, 1154, 1497.
688. E. Heber, *Brit. pat.* 10,004 of 1903.
689. L. E. Hebl, T. B. Rendel, and F. L. Garton, *Ind. Eng. Chem.*, 25, 187-91 (1933)—C.A. 27, 1493.
690. W. O. Heilmann to S. O. Dev. Co., (a) U.S. pat. 2,273,104 (1942); (b) 2,324,927 (1943)—C.A. 36, 4327; 38, 482.
691. G. H. Hellsing, *Brit. pat.* 9,180 of 1907—C.A. 2, 487.
692. T. Hellthaler, (a) U.S. pat. 1,643,272 (1927); (b) 1,645,530 (1927)—C.A. 21, 3739; 22, 162.
693. R. V. Helm, W. E. Haines, and J. S. Ball, U.S. Bur. Mines Rept. Investigations, 4566 (1949).
694. C. J. Helmers and G. M. Brooner, *Petroleum Processing*, 3, 133-8 (1948)—C.A. 42, 9142.
695. L. M. Henderson to Atlantic Refg. Co., U.S. pat. 1,940,861 (1933)—C.A. 28, 1521.
696. L. M. Henderson to Pure Oil Co., U.S. pat. 2,317,053 (1943)—C.A. 37, 6121.
697. L. M. Henderson, M. S. Agruss, and G. W. Ayers, Jr., *Anal. Chem.*, 12, 1-3 (1940)—C.A. 34, 1604.
698. L. M. Henderson and G. W. Ayers, Jr., to Pure Oil Co., (a) U.S. pat. 2,292,636 (1942); (b) 2,297,621 (1942); (c) 2,312,820 (1943); (d) 2,317,054 (1943); (e) 2,341,917 (1944)—C.A. 37, 1260, 1860, 5581, 6121; 38, 5076.
699. L. M. Henderson, G. W. Ayers, Jr., and D. C. Bond to Pure Oil Co., U.S. pat. 2,317,055 (1943)—C.A. 37, 6120.
700. L. M. Henderson, G. W. Ayers, Jr., and Timothy McNamara to Pure Oil Co., U.S. pat. 2,341,918 (1944)—C.A. 38, 5076.
701. L. M. Henderson, G. W. Ayers, Jr., and C. M. Ridgway, *Oil Gas J.*, 38, No. 46, 114, 118, 121 (1940)—C.A. 34, 4551.
702. L. M. Henderson and D. C. Bond to Pure Oil Co., U.S. pat. 2,317,056 (1943)—C.A. 37, 6120.

703. L. M. Henderson and H. C. Cowles, Jr., to Atlantic Refg. Co., U.S. pat. 1,815,563 (1931)—C.A. 25, 5551.
704. L. M. Henderson, W. B. Ross, and C. N. Ridgway, Ind. Eng. Chem., 31, 27–30 (1939)—C.A. 33, 1128.
705. L. M. Henderson and Arthur Schroder to Pure Oil Co., U.S. pat. 2,297,620 (1942)—C.A. 37, 1859.
706. A. Henriksen, Natl. Petr. News, 19, No. 42, 64–8 (1927); Refiner Natural Gasoline Mfr., 6, No. 10, 51–2, 93 (1927); Oil Gas J., 26, No. 21, 130–1 (1927)—C.A. 22, 158.
707. C. Henry, Brit. pat. 1,664, of 1898; Ger. pat. 107,239 (1898)—C. 1900, I, 840.
708. L. Henry, Ber., 2, 495–7 (1869).
709. O. Henry, J. prakt. Chem., 46, 160–2 (1847).
710. R. W. Henry, J. A. Reid, and W. A. Schulze to Phillips Petroleum Co., U.S. pat. 2,089,373 (1937)—C.A. 31, 7242.
711. Harry Hepworth and H. W. Clapham, J. Chem. Soc., 119, 1188–91 (1921)—C.A. 15, 3088.
712. S. M. Herber, U.S. pat. 1,111,580 (1914)—C.A. 8, 3628.
713. S. H. Herglotz and A. Lissner, (a) Z. anorg. Chem., 260, 141–53 (1949); (b) *ibid.*, 261, 237–47 (1950)—C.A. 44, 10474.
714. F. Hermann, Ber., 38, 2814 (1905).
715. D. A. Hermanson and J. L. Biles to Socony-Vac. Oil Co., U.S. pat. 2,537,999 (1951)—C.A. 46, 2288.
716. P. R. Hershman, U.S. pat. 2,064,541 (1936)—C.A. 31, 850.
717. E. C. Herthel to Sinclair Refg. Co., (a) U.S. pat. 1,733,800 (1929); (b) 1,772,865 (1930)—C.A. 24, 496, 5147.
718. Jean Herzenberg, Erdöl u. Teer, 9, 436–9, 448–51 (1933); Brit. pat. 424,564 (1935)—C.A. 28, 3566; 29, 5260.
719. Jean Herzenberg and S. Ruhemann, Braunkohle, 26, No. 23/24, 526–32, 558–64 (1927).
720. R. W. Hess to Barrett Co., Can. pat. 313,447 (1931); U.S. pat. 1,904,461 (1933)—C.A. 25, 4510; 27, 3436.
721. F. Heusler, (a) Z. angew. Chem., 9, 318–321 (1896); (b) Ger. pat. 83,494 (1894)—C. 1895, II, 1142.
722. H. H. Hewetson, Oil Gas J., 27, No. 29, 118, 181, 182 (1928)—C.A. 23, 2281.
723. A. P. Hewlett to S. O. Dev. Co., (a) U.S. pat. 2,218,610 (1940); (b) 2,316,691 (1943); (c) 2,336,174 (1943); (d) 2,337,467 (1943)—C.A. 35, 1624; 37, 6121; 38, 3825.

- 724. A. P. Hewlett and H. C. Paulsen to S. O. Dev. Co., (a) U.S. pat. 2,348,623 (1944); (b) 2,428,623 (1947)—C.A. 39, 806; 42, 749.
- 725. A. P. Hewlett and G. E. Phillips to S. O. Dev. Co., U.S. pat. 2,391,091 (1945)—C.A. 40, 1025.
- 726. W. G. Hiatt, *Oil Gas J.*, 23, No. 48, 22-3, 175 (1925); *Natl. Petr. News*, 17, No. 16, 26-9 (1925)—C.A. 19, 1943.
- 727. W. Hieber and P. Spacu, *Z. anorg. allgem. Chem.*, 233, 353-64 (1937)—C.A. 31, 8411.
- 728. E. C. Higgins, Jr., and F. T. Gardner, U.S. pat. 1,977,631 (1934)—C.A. 29, 334.
- 729. H. M. Hill and M. L. Wolfrom, *J. Am. Chem. Soc.*, 69, 1539 (1947)—C.A. 41, 5851.
- 730. J. B. Hill to Atlantic Refg. Co., U.S. pat. 1,667,550, 1,682,562 (1928)—C.A. 22, 2054, 3985.
- 731. E. S. Hillman to Anglo-Saxon Petroleum Co., *Brit. pat.* 214,733 (1923)—C.A. 18, 2804.
- 732. J. H. Hirt to L. J. Hirt, U.S. pat. 1,809,554 (1931); 1,910,288 (1933)—C.A. 25, 4395; 27, 4070.
- 733. L. E. Hirt, U.S. pat. 1,250,879 (1917)—C.A. 12, 531.
- 734. W. G. Hockberger to S. O. Dev. Co., U.S. pat. 2,469,726 (1949)—C.A. 43, 5584.
- 735. W. H. Hoffert and G. Claxton, *Fuel in Science & Practice*, 9, 359-66, 440-7, 476-81 (1930)—C.A. 24, 5967.
- 736. W. H. Hoffert and K. Wendtner, *J. Inst. Petroleum*, 35, 171-92 (1949)—C.A. 43, 5932.
- 737. W. S. Hoffman and E. E. Reid, *J. Am. Chem. Soc.*, 45, 1831-8 (1923)—C.A. 17, 3338.
- 738. A. W. von Hofmann, *Ber.*, 4, 163 (1871).
- 739. A. W. von Hofmann and Auguste Cahours, *J. Chem. Soc.*, 10, 320 (1858).
- 740. Fritz Hofmann and Robert Uloth, *Brit. pat.* 306,421 (1929); *Ger. pat.* 595,349 (1934)—C. 1929, II, 963; C.A. 28, 4213.
- 741. K. A. Hofmann and W. O. Rabe, (a) *Z. anorg. Chem.*, 14, 293-6 (1897); (b) *ibid.*, 17, 26-34 (1898).
- 742. K. A. Hofmann and O. F. Wiede, *Z. anorg. Chem.*, 9, 295-303 (1895).
- 743. H. Hofmeier and S. Wisselinck, (a) *Brennstoff-Chem.*, 14, 101-3 (1933); (b) *ibid.*, 286-8—C.A. 27, 3802, 5933.
- 744. H. Hofmeier, S. Wisselinck, and A. Müller, *Angew. Chem.*, 47, 513-5 (1934)—C.A. 28, 6289.

745. Max Hofsass and Internationale Bergin Comp. voor Olie-en-Kolen Chemie, Brit. pat. 213,661 (1923); U.S. pat. 1,729,943 (1929)—C.A. 18, 2426; 23, 5568.
746. W. W. Holland to Petroleum Conversion Corp., U.S. pat. 2,125,636 (1938)—C.A. 32, 7715.
747. H. Hollings, Inst. Gas Engrs., Copyright Pub. No. 175/64; 4-7, 51-64 (1937); Gas. J., 220, 475-6, 479-85, 667; Gas World, 107, 379-83, 471-6, 563—C.A. 32, 6437.
748. C. Holloway, Jr., and W. S. Bonnell, Ind. Eng. Chem., 37, 1089-91 (1945)—C.A. 40, 1303.
749. F. A. L. Holloway and D. O. Wilkes to S. O. Dev. Co., U.S. pat. 2,317,770 (1943)—C.A. 37, 6447.
750. Bror Holmberg, (a) Ann., 359, 81-99 (1908); (b) Ber., 43, 226-7 (1910); (c) Arkiv Kemi, Mineral. Geol., 12A, No. 14, 10 p. (1937); (d) *ibid.*, 12B, No. 17, 3 p. (1938); (e) *ibid.*, 13A, No. 8, 9 p. (1939)—C.A. 2, 1690; 4, 1047; 31, 4292; 32, 4151; 33, 6278.
751. A. Holmes and L. Burgess, U.S. pat. 1,832,461 (1931)—C.A. 26, 1114.
752. H. N. Holmes, U.S. pat. 1,882,146 (1932)—C.A. 27, 593.
753. H. N. Holmes and Norvil Beeman, Ind. Eng. Chem., 26, 172-4 (1934)—C.A. 28, 1697.
754. H. N. Holmes, A. L. Elder, and Norvil Beeman, J. Phys. Chem., 36, 2981-93 (1932)—C.A. 27, 1491.
755. W. C. Holmes & Co. Ltd., Charles Cooper, and J. J. Priestley, Brit. pat. 593,253 (1947)—C.A. 42, 1412.
756. Ronald Holroyd, D. H. P. Peel, and Imp. Chem. Ind., Brit. pat. 577,813 (1946)—C.A. 41, 2236.
757. J. C. Holtz, The Origin and Decomposition of Organic Sulfur Compounds under Gas-Making Conditions with Particular Reference to the Role of the C-S Complex, Johns Hopkins Univ., 83 p.—Reviewed, Ind. Eng. Chem., 22, 1261 (1930).
758. Lee Holtz, Gas-Age Record, 66, 341-5 (1930)—C.A. 24, 5977.
759. Holzverkohlungs-Ind. A. G. and J. Varga, Brit. pat. 313,505 (1929)—C. 1930, I, 2666.
760. J. J. Hood, (a) Brit. pat. 145,818 (1919); (b) U.S. pat. 1,404,293, 1,404,294 (1922)—J. Soc. Chem. Ind., 39, 651A (1920); C.A. 16, 1148.
761. J. J. Hood and Oil Refining Improvements Co., Ltd., Japan. pat. 35,796 (1920)—C.A. 14, 3788.
762. J. J. Hood and A. G. Salamon to Oil Refining Improvements Co., U.S. pat. 962,840 (1910)—C.A. 4, 2568.

- 762.5. H. Hoog, *Rec. trav. chim.*, **69**, 1289–96 (1950)—C.A. **45**, 4435.
763. C. O. Hoover, *Petroleum Refiner*, **27**, 355–9 (1948)—C.A. **42**, 7963.
764. C. O. Hoover to Air Reduction Co., (a) U.S. pat. 2,329,615, 2,329,616 (1943); (b) 2,418,884 (1947); (c) 2,423,238, 2,430,981, 2,430,982 (1947); 2,455,061 (1948)—C.A. **38**, 1352; **41**, 7103, 6398; **42**, 1415, 1412; **44**, 4237.
765. C. O. Hoover to Bennett-Clark Co., (a) U.S. pat. 2,042,050, 2,042,051, 2,042,052, 2,042,053, 2,042,054 (1936); Reissue 20,938 (1938); (b) 2,042,055 (1936)—C.A. **30**, 5024; **33**, 2321; **30**, 5024.
766. J. Houben and Hans Doescher, *Ber.*, **39**, 3503–9 (1906)—C.A. **1**, 304.
767. E. J. Houdry to Houdry Process Corp., U.S. pat. 2,259,469 (1941)—C.A. **36**, 892.
768. E. J. Houdry, W. F. Burt, A. E. Pew, Jr., and W. A. Peters, Jr., *Oil Gas J.*, **37**, No. 28, 40–3, 45, 48 (1938); *World Petroleum*, **9**, No. 11, 68–71, 132, 134; *Natl. Petroleum News*, **30**, R570–2, 574, 576–80; *Refiner Natural Gasoline Mfr.*, **17**, 574–82, 619—C.A. **33**, 4005.
769. W. R. Hounsell, *Natl. Petr. News*, **20**, No. 1, 83–6 (1928); *Refiner Nat. Gasoline Mfr.*, **7**, No. 3, 59–60, 112 (1928); *Oil Gas J.*, **27**, No. 44, 34 (1929)—C.A. **23**, 3336.
770. Theo van Hove, *Bull. soc. chim. Belg.*, **13**, 206–24 (1927)—C.A. **22**, 62.
771. R. D. Howard to Petroleum Research Corp., (a) U.S. pat. 2,205,410 (1940); (b) 2,338,941 (1944)—C.A. **34**, 7593; **38**, 4430.
772. H. F. Howell, *Brit. pat.* 2,410 of 1879; U.S. pat. 216,518 (1879).
773. H. Hubner and Julius Alsberg, *Ann.*, **156**, 308–32 (1870).
774. T. B. Hudson and J. O. Turner to Phillips Petroleum Co., U.S. pat. 2,371,298 (1945)—C.A. **39**, 4471.
775. Hugo Hütz, *Ger. pat.* 374,928, 385,761, 387,593 (1923)—C. **1923**, IV, 346; **1924**, I, 1132, 1133.
776. W. J. Huff, *Proc. 2nd Intern. Conference Bituminous Coal*, **2**, 814–5 (1928)—C.A. **23**, 4047.
777. W. J. Huff and Lloyd Logan, *Am. Gas. Assoc., Proc.*, **18**, 724–33, 733–52, 754–9 (1937)—C.A. **31**, 5134.
778. J. R. Huffman and J. M. Whiteley, Jr., U.S. pat. 1,995,612 (1935)—C.A. **29**, 2976.
779. E. C. Hughes to S. O. Co. of Ohio, (a) U.S. pat. 2,148,470 (1939); (b) 2,211,695 (1940)—C.A. **33**, 3980; **35**, 586.

780. E. C. Hughes, W. E. Scovill, C. H. Whitacre, R. B. Faris, J. D. Bartleson, and S. M. Darling, ACS Meeting, Houston, Tex., March 26–30, 1950.
781. Huiles, Goudrons et Derivés, Fr. pat. 601,172 (1926)—C. 1926, II, 149.
782. S. H. Hulse to S. O. Dev. Co., U.S. pat. 2,402,893 (1946)—C.A. 40, 6247.
783. S. H. Hulse and J. O. Collins to S. O. Dev. Co., U.S. pat. 2,288,401 (1942)—C.A. 37, 525.
784. E. Human, Ann. chim. phys., [3] 44, 337 (1855); Ann., 95, 256 (1855).
785. E. B. Hunn to S. O. Dev. Co., U.S. pat. 1,786,246 (1930)—C.A. 25, 588.
786. J. B. Huston, U.S. pat. 486,406 (1892).
787. W. K. Hutchison, Inst. Gas Engrs., Copyright Pub. 175/64; 8–44, 51–64; Gas. J., 220, 475–6, 479–85, 667; Gas World, 107, 379–83, 471–6, 563—C.A. 32, 6437.
788. E. M. Hyatt, U.S. pat. 1,445,688 (1923)—C.A. 17, 1547.
789. I. G. Farben., (a) Australian pat. 17,448 (1928); Brit. pat. 327,194 (1930); (b) 247,584, 247,585 (1926); 348,690 (1931); (c) 333,511 (1930); (d) 364,655 (1932); Fr. pat. 717,301 (1932)—C. 1930, I, 2667; C.A. 24, 5150; C. 1926, II, 2256; 1931, II, 1233, I, 194; 1932, II, 485.
790. I. G. Farben., (a) Brit. pat. 315,439 (1930); (b) 320,921 (1928); (c) 340,016 (1929); (d) 365,619 (1930)—C.A. 24, 1734, 2595; 25, 2838; 27, 1738.
791. I. G. Farben., (a) Fr. pat. 655,230 (1928); (b) Brit. pat. 300,900 (1927); 327,463 (1928); 345,738 (1931)—C.A. 23, 3934, 4061; 24, 5149; 26, 589.
792. I. G. Farben., (a) Brit. pat. 274,828 (1927); (b) 276,427 (1926); (c) 321,406 (1928); (d) 340,470 (1929)—B.A. 1928, 702B; C.A. 22, 2462; 24, 2821; 25, 4108.
793. I. G. Farben., (a) Fr. pat. 652,243 (1928); (b) 772,002 (1934); Brit. pat. 361,357 (1930); 435,113 (1935)—C.A. 23, 3523; 29, 1436; 27, 1890; 30, 1068.
794. I. G. Farben., (a) Ger. pat. 705,850 (1930); (b) Brit. pat. 362,964 (1930); (c) 465,291 (1937)—C.A. 26, 329; 27, 1535; 33, 3810.
795. I. G. Farben., (a) Fr. pat. 767,044 (1934); (b) 843,903 (1939); Brit. pat. 519,730 (1940); (c) 497,939 (1938)—C.A. 29, 2655; 34, 7143; 36, 295; 33, 3810.
796. I. G. Farben., (a) Brit. pat. 291,817 (1927); (b) Ger. pat. 708,933 (1941); (c) Belg. pat. 451,249 (1943)—C.A. 23, 1190; 37, 3252; 42, 586.

797. I. G. Farben. (Max Bockmühl, Walter Persch, and Walter Kross), Ger. pat. 565,064 (1930)—C.A. 27, 1093.
798. I. G. Farben. (F. A. Henglein and Hermann Hagenest), Ger. pat. 558,940 (1927)—C.A. 27, 543.
799. I. G. Farben. (Karl Keller), Ger. pat. 557,245, 559,739 (1930)—C.A. 27, 310, 730.
800. I. G. Farben. (Martin Luther and Kurt Pieroh), Ger. pat. 471,076 (1926)—C.A. 23, 2313.
801. I. G. Farben. (Alvin Mittasch and Wilhelm Pungs), Ger. pat. 556,369 (1921)—C.A. 26, 5749.
802. I. G. Farben. (Friedrich Muth), Ger. pat. 564,043 (1932)—C.A. 27, 1204.
803. I. G. Farben. (Ludwig Orthner and Ewald Zaucker), Ger. pat. 651,763, 651,811 (1937)—C.A. 32, 834.
804. I. G. Farben. (Wilhelm Pungs), Ger. pat. 455,522 (1921)—C. 1928, I, 2330.
805. I. G. Farben. (Wilhelm Pungs and Ernst Galle), Ger. pat. 453,883 (1927)—C. 1928, I, 1125.
806. I. G. Farben. (Walter Reppe and Fritz Nicolai), (a) Ger. pat. 617,543 (1935); 624,845 (1936); (b) 631,016 (1936)—C.A. 30, 733, 4871, 6008.
807. I. G. Farben. (Edward Tschunkur and Ernest Herdieckerhoff), Ger. pat. 565,967 (1930)—C.A. 27, 2538.
808. I. G. Farben. (Hans Ufer), Ger. pat. 528,915 (1926)—C.A. 26, 1045.
809. I. G. Farben. (Gustav Wietzel, Josef Jannek, and Fritz Fried), Ger. pat. 476,286 (1927)—C.A. 23, 3797.
810. H. K. Ihrig to Associated Oil Co., U.S. pat. 1,712,619 (1929)—C.A. 23, 3340.
811. Imp. Chem. Ind., Ltd., Brit. pat. 520,505 (1940)—C.A. 36, 595.
812. Imperial Oil, Ltd., Brit. pat. 305,108 (1929)—C.A. 23, 4814.
813. Internationale Bergin Compagnie voor Olie-en Kolen Chemie, Dutch pat. 13,594 (1925); Fr. pat. 559,787, 632,509 (1926)—C.A. 20, 495; 22, 3773.
814. International Hydrogenation Patents Co. Ltd., Fr. pat. 774,343 (1934)—C.A. 29, 2338.
815. Vladimir Ipatieff to U. O. Prods. Co., U.S. pat. 2,037,789, 2,037,790, 2,037,791, 2,037,792 (1936)—C.A. 30, 4000.
816. V. N. Ipatieff and B. S. Friedman, J. Am. Chem. Soc., 61, 71-4 (1939)—C.A. 33, 1659.

817. V. N. Ipatieff, G. S. Monroe, and R. E. Schaad, ACS Meeting, San Francisco, March 27–April 1, 1949; Houston, March 26–30 (1950).
818. E. P. Irary and H. D. Noether to Celanese Corp., U.S. pat. 2,481,596 (1949)—C.A. 43, 9527.
819. E. Iwase, *Kolloid Z.*, 45, 31–6 (1928)—C.A. 22, 3081.
820. C. L. Jackson and A. Oppenheim, *Ber.*, 8, 1032–4 (1875).
821. T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, 61, 442–50 (1939)—C.A. 33, 2498.
822. F. Jardine, *J. Soc. Automotive Engrs.*, 17, 605–6 (1925).
823. A. R. Javes, *J. Inst. Petroleum*, 31, 129–53, 343–6 (1945)—C.A. 39, 3902; 40, 2964.
824. W. P. Jenney, U.S. pat. 178,061 (1876).
825. J. M. Jennings to S. O. Dev. Co., *Brit. pat.* 360,201 (1930)—C.A. 27, 593.
826. K. A. Jensen, *Z. anorg. Chem.*, 252, 227–33 (1944)—C.A. 40, 4352.
- 826.5. J. Jiminez-Herrera and L. Bermejo, *Anales soc. espan. fis. quim.*, 31, 267–70 (1933)—C.A. 27, 2908.
827. E. M. Johansen, (a) U.S. pat. 1,587,649 (1926); (b) 1,601,216 (1926)—C.A. 20, 2583, 3799.
828. Axel Johansson, (a) *Arkiv Kemi, Mineral Geol.*, 13A, No. 14, 11 p. (1939); (b) *ibid.*, 24A, No. 30, 12 p. (1947)—C.A. 33, 8467; 42, 5409.
829. Johnson, *Chem. Trade J.*, 19, 476 (1896).
830. A. J. Johnson to Shell Dev. Co., U.S. pat. 2,368,595 (1945)—C.A. 39, 5440.
831. H. R. Johnson, U.S. pat. 2,348,543 (1944)—C.A. 39, 806.
832. J. Y. Johnson, *Brit. pat.* 8,348 of 1896.
833. S. E. Johnson and E. E. Johnson, *Brit. pat.* 5255 of 1875.
834. J. J. Johnston, U.S. pat. 31,982 (1861); 91,447 (1869).
835. L. M. Johnston and J. L. Farrell, U.S. pat. 1,706,614 (1929)—C.A. 23, 2290.
836. W. W. Johnstone to U. O. Prods. Co., (a) U.S. pat. 2,185,768 (1940); 2,258,249 (1941); (b) 2,318,495 (1943); (c) 2,593,761 (1952)—C.A. 34, 3070; 36, 892; 37, 6447; 46, 7756.
837. E. M. Jolly and C. C. Swoope, U.S. pat. 1,934,068 (1933)—C.A. 28, 631.
838. H. O. Jones and J. K. Matthews, *Proc. Camb. Phil. Soc.*, 15, 529–30—C.A. 5, 1237.
839. J. P. Jones to Phillips Petroleum Co., U.S. pat. 2,376,060 (1945)—C.A. 39, 4468.

840. M. C. K. Jones to S. O. Dev. Co., (a) U.S. pat. 2,270,058 (1942); 2,319,738 (1943); (b) 2,372,084 (1945); (c) 2,420,544 (1947); (d) 2,440,673 (1948)—C.A. 36, 3953; 37, 6880; 40, 455; 41, 7105; 42, 8456.
841. M. C. K. Jones and R. C. Brandon to S. O. Dev. Co., (a) U.S. pat. 2,320,277 (1943); (b) 2,338,585 (1944)—C.A. 37, 6880; 38, 4429.
842. Alexandre Joseph, *Rev. chim. ind.*, 36, 16 (1927)—C.A. 21, 1346.
843. P. M. Justice to Allgem. Ges. f. Chem. Ind., *Brit. pat.* 3572 of 1914—*J. Soc. Chem. Ind.*, 34, 1004 (1915).
844. Herman Kahn, *Bull. soc. chim. Roumania*, 5, 70-2 (1923)—C.A. 18, 1467.
845. V. A. Kalichevsky, (a) *Petroleum Refiner*, 24, No. 4, 89-91 (1945); (b) No. 9, 89-94 (1945).
846. V. A. Kalichevsky, (a) *Petroleum Refiner*, 29, No. 11, 97-100 (1950); (b) *ibid.*, No. 12, 113-5; (c) *ibid.*, 30, No. 1, 129-35 (1951); (d) *ibid.*, No. 2, 95-6; (e) *ibid.*, No. 3, 122-5; (f) *ibid.*, No. 4, 111-8; (g) *ibid.*, No. 5, 117-22; (h) *ibid.*, No. 6, 135-7—C.A. 45, 1756, 2183, 3151, 4434, 5395, 6372, 6828, 8239.
847. V. A. Kalichevsky, *Modern Methods of Refining Lubricating Oils*, New York, Reinhold, 1938.
848. Vladimir Kalichevsky to S. O. Dev. Co., U.S. pat. 2,028,335 (1936)—C.A. 30, 1549.
849. V. A. Kalichevsky, E. T. Scafe, and K. F. Hayden to Socony-Vac. Oil Co., U.S. pat. 2,311,593 (1943)—C.A. 37, 4890.
850. V. A. Kalichevsky and B. A. Stagner, *Chemical Refining of Petroleum*, New York, Reinhold, 1942.
851. E. D. Kamm, Basil Taffs, and Imp. Chem. Inds. Ltd., *Brit. pat.* 404,960 (1934)—C.A. 28, 4589.
852. Takeo Kaneko, *J. Chem. Soc. Japan*, 59, 1139-41 (1938)—C.A. 33, 2105.
853. J. H. Karchmer and J. W. Dunahoe, *Anal. Chem.*, 20, 915-9 (1948)—C.A. 43, 8123.
- 853.5. Clarence Karr, *Anal. Chem.*, 26, 528-36 (1954)—C.A. 48, 7499.
854. M. L. Kastens and Robert Sutherland, *Ind. Eng. Chem.*, 42, 582-93 (1950)—C.A. 44, 5085.
855. H. L. Kauffman and I. A. Clark to H. L. Kauffman, U.S. pat. 1,684,035 (1928)—C.A. 22, 4241.

856. A. Kayser, (a) U.S. pat. 508,479 (1893); (b) 640,918 (1900).
857. E. I. Kazukov, N. G. Edelstein, and A. F. Tchegis, *Bull. acad. sci. URSS, Classe sci. Tech.*, 1946, 1621-8; *Dept. Sci. Ind. Research (Brit.)*, *Fuel Abstracts*, 2, No. 1, 38 (1947)—C.A. 41, 3605; 42, 5650.
858. W. O. Keeling, U.S. pat. 2,150,170 (1939)—C.A. 33, 4779.
859. August Kekulé and Linnemann, *Ann.*, 123, 279 (1862).
860. C. H. Keller to Minerals Sepn. N. A. Corp., U.S. pat. 1,728,764 (1929)—C.A. 23, 5148.
861. E. D. Kendall, U.S. pat. 451,660 (1891).
862. D. M. Kennedy, *Brit. pat.* 6,018 of 1887; U.S. pat. 370,950 (1887); *Ger. pat.* 43,145 (1888).
- 862.5. R. J. Kern, *J. Am. Chem. Soc.*, 75, 1865-6 (1953)—C.A. 48, 4462.
863. H. L. Kerr to Frank Gardner, U.S. pat. 2,053,909 (1936)—C.A. 30, 7833.
864. A. L. Khalif and L. B. Samoilov, *Azerbaidzhanskoe Neftyanoe Khoz.*, 1939, No. 12, 31-2—C.A. 35, 3421.
- 864.5. M. S. Kharasch, W. Nudenberg, and G. J. Mantell, *J. Org. Chem.*, 16, 524-32 (1951)—C.A. 46, 1483.
865. K. V. Kharichkov, (a) *J. der Kakt.—Abtheil der K. Russ. tech. G.*, 1897, 272; (b) *Westnik shirow. promysl.*, 7, 61 (1906)—*Z. angew. Chem.*, 11, 86-7 (1898); *Chem. Ztg.*, 30, Rep. 205 (1906).
866. Hugo Kiemstedt, *Oel u. Kohle*, 39, 833 (1943)—C.A. 38, 5388.
867. Hugo Kiemstedt, *Ger. pat.* 640,204 (1936)—C.A. 31, 2410.
868. E. Kiene, *Vorratspflege u. Lebensmittelforsch.*, 2, 698-706 (1939)—C.A. 35, 7002.
869. F. E. Kimball, (a) U.S. pat. 1,892,801 (1933); (b) 1,895,223 (1933); (c) 2,108,438 (1938); 2,171,033 (1939); (d) 2,121,169 (1938)—C.A. 27, 2294, 2572; 32, 3140; 34, 255; 32, 6453.
870. J. W. Kimball, R. L. Kramer, and E. E. Reid, *J. Am. Chem. Soc.*, 43, 1199-1200 (1921)—C.A. 15, 2881.
871. T. B. Kimball, *Brit. pat.* 291,379 (1927)—C.A. 23, 1260.
872. T. B. Kimball to Shell Oil Co., U.S. pat. 1,831,916 (1931)—C.A. 26, 837.
873. H. L. King, Jr., C. D. Laughlin and H. M. Gwyn, Jr., *Oil Gas J.*, 42, No. 49, 236, 239, 241, 244; No. 50, 51-74 (1944)—C.A. 38, 4416.

874. H. S. King and F. B. Maddock, *Can. Chem. Process Inds.*, 23, 3-4 (1939)—C.A. 33, 2312.
875. R. O. King, *Can. J. Research*, 26F, 125-50 (1948)—C.A. 42, 5651.
876. A. Kinsel, *Chem. Met. Eng.*, 32, 873-4 (1925); U.S. pat. 1,525,301 (1925); 1,883,947 (1932); Brit. pat. 263,730 (1925)—C.A. 20, 661; 19, 1049; 27, 1157; 22, 162.
877. J. L. Kirk, U.S. pat. 215,756 (1879).
878. M. L. Kirk to M. P. Kirk & Son, Inc., U.S. pat. 1,977,993 (1933)—C.A. 29, 329.
879. R. Kissling, *Chem. Ztg.*, 32, 849, 867, 879—C.A. 3, 589.
880. R. Kissling, *Das Erdöl, seine Verarbeitung und Verwendung*, Halle, 1908.
881. Peter Klason, (a) *Bull. soc. chim.* [2] 25, 183-7 (1876); (b) *J. prakt. Chem.*, [2] 15, 193-218 (1877); (c) *Ber.*, 14, 411-2 (1881); (d) *ibid.*, 20, 3407-13 (1887).
882. Peter Klason and Tor Carlson, *Ber.*, 39, 738-42 (1906).
883. Willi Klatt, *Z. anorg. allgem. Chem.*, 232, 393-409 (1937)—C.A. 31, 5705.
884. Morton Kleiman to Velsicol Corp., U.S. pat. 2,510,893, 2,510,894 (1950)—C.A. 45, 636, 637.
885. E. N. Klemgard, *Refiner Natural Gasoline Mfr.*, 6, No. 5, 51-2 (1927)—C.A. 21, 2788.
886. H. W. Klever, (a) *Ger. pat.* 301,773 (1921); (b) 368,740 (1923)—C. 1921, IV, 212; 1923, II, 878.
887. A. Klinkenberg, *Oel u. Kohle ver. petroleum*, 35, 709-12 (1939)—C.A. 34, 4260.
888. N. V. S. Knibbs, *Brit. pat.* 154,464 (1919)—*J. Soc. Chem. Ind.*, 40, 38A (1921).
889. H. W. Knottenbelt, U.S. pat. 1,194,033 (1916)—C.A. 10, 2402.
890. W. M. Knowling (Michael Kostevitch), *Fr. pat.* 651,641 (1928)—C.A. 23, 3339.
891. W. M. Knowling and Michael Kostevitch, (a) *Brit. pat.* 287,141 (1927); *Fr. pat.* 641,926 (1927); (b) *Brit. pat.* 308,604 (1928)—C.A. 23, 510, 1259; 34, 496.
892. G. P. Koch to Shell Oil Co., U.S. pat. 1,742,263 (1930)—C.A. 24, 1212.
893. H. Koehler, U.S. pat. 507,441 (1893).
894. Kohle u. Eisenforschung G.m.b.H., *Brit. pat.* 491,299 (1938)—C.A. 33, 1478.
895. E. P. Kohler, *Am. Chem. J.*, 22, 67-80 (1899).

896. Toshio Kojima, Takeo Yamamuro, and Tosaburo Sahan to Hodogaya Chem. Ind. Co., Japan. pat. 175,175 (1947)—C.A. 44, 5913.
897. G. Kolsky, U.S. pat. 1,598,973 (1926)—C.A. 20, 3563.
898. Eric Kolthoff and A. E. Catanach to Gulf Oil Corp., U.S. pat. 2,250,915 (1941)—C.A. 35, 7703.
- 898.5. I. M. Kolthoff and W. J. Dale to Phillips Pet. Co., U.S. pat. 2,625,537 (1953)—C.A. 47, 7249.
899. I. M. Kolthoff and W. E. Harris (a) *J. Polymer Sci.*, 2, 41–8, 49–71 (1947); (b) *Anal. Chem.*, 18, 161–2 (1946); (c) *ibid.*, 21, 963–5 (1949)—C.A. 41, 4957; 40, 3370; 44, 76.
900. I. M. Kolthoff, D. R. May, Perry Morgan, H. A. Laitiner, and A. S. O'Brien, *Anal. Chem.*, 18, 442–4 (1946)—C.A. 40, 5359.
901. I. M. Kolthoff and I. K. Miller, *J. Am. Chem. Soc.*, 73, 5118–22 (1951), 74, 4419–22 (1952)—C.A. 46, 1853; 47, 63.
902. V. I. Komarewsky and E. A. Knaggs, *Ind. Eng. Chem.*, 43, 1414–8 (1951)—C.A. 46, 490.
903. M. S. Komsii, *Neftyanoe Khoz.*, 1937, No. 7, 49–53—C.A. 33, 7086.
904. Fritz von Konek, *Ber.*, 53, 1666–71 (1920)—C.A. 15, 845.
905. T. A. Kontorova and M. B. Neumann, *Physik. Z. Sowjetunion*, 4, 818–24 (1933)—C.A. 28, 2979.
906. R. D. Koons, *Refiner Natural Gasoline Mfr.*, 20, 393 (1941)—C.A. 36, 1474.
907. Hermann Kopp, *Ann.*, 35, 343–50 (1840).
908. E. L. Korb and J. R. Sabina to Du Pont Co., U.S. pat. 2,380,976 (1945)—C.A. 40, 729.
909. D. N. Korotchenko and P. I. Tsyganok, *Neftyanoe Khoz.*, 19, No. 7, 21–5 (1938)—C.A. 33, 1917.
- 909.5. M. M. Koton, E. P. Moskvina, and F. S. Florinskii, *J. Gen. Chem. (USSR)*, 20, 2093–5, 2167–9 (English translation) (1950)—C.A. 45, 5644; 46, 11135.
910. M. H. Kotzebue and L. M. Bowman, U.S. pat. 1,485,083 (1924)—C.A. 18, 1383.
911. A. V. Kozhevnikov and I. Y. Grachev, *J. Applied Chem. (USSR)*, 11, 962–4 (1938)—C.A. 33, 1920.
912. A. J. Kraemer, *Bur. Mines, Rept. of Investigations*, 3026, 11 p. (1930); *Oil Gas J.*, 29, No. 8, 31 (1930)—C.A. 24, 3878.
913. H. I. Kramer, *Ind. Eng. Chem.*, 34, 243 (1942).

914. Carl Krauch, Mathias Pier, and Karl Winkler to Standard-I. G. Co., U.S. pat. 1,957,787 (1934)—C.A. 28, 4216.
915. P. L. Krauel and G. W. Watts, U.S. pat. 1,936,629 (1933)—C.A. 28, 1179.
916. William Krause, *Chemist-Analyst*, 27, No. 1, 14 (1938)—C.A. 32, 2722.
917. Krausz-Moskovits Egyesült Ipartelepek R. T. and Miklos Moskovits, Hung. pat. 102,737 (1928)—C.A. 26, 1703.
918. A. Kremser, *Natl. Pet. News*, 22, No. 21, 43-9 (1930); *Oil Gas J.*, 29, No. 1, 146, 148, 150, 178 (1930)—C.A. 24, 5143, 3328.
919. O. Kruber and W. Schade, *Brennstoff-Chem.*, 14, 124-8 (1933)—C.A. 27, 3802.
920. R. C. Krug to Atlantic Refg. Co., U.S. pat. 2,441,493 (1948)—C.A. 42, 8462.
921. Hermann Krutzsch, *J. prakt. Chem.*, 31, 1-4 (1844); *Ann.*, 52, 317-9 (1844).
922. Richard Kuhn, Leonard Birkofer, and F. W. Quackenbush, *Ber.*, 72, 407-16 (1939)—C.A. 33, 4625.
923. M. Kuras, *Chem. Obzor*, 16, 17-8, 124-5 (1941); 17, 41 (1942); 18, 177-8 (1943)—C.A. 38, 933; 37, 3023; 39, 3222.
924. E. W. Laake, D. C. Parman, F. C. Bishopp, and R. C. Roark, U.S. Dept. Agr. Tech. Bull., 270, 10 p. (1931)—C.A. 26, 4882.
925. Arthur Lachman, *Ind. Eng. Chem.*, 23, 354-7 (1931)—C.A. 25, 2553.
926. Arthur Lachman, *Oil Gas J.*, 30, No. 26, 30, 133-5 (1931); *Natl. Petroleum News*, 23, No. 45, 32-E-33, 35; *Petroleum World*, 28, No. 11, 23-5, 46; No. 12, 41-3 (1931); *Refiner Natural Gasoline Mfr.*, 10, No. 11, 72 (1931)—C.A. 26, 1425, 2044, 5408, 3097.
927. Arthur Lachman to Richfield Oil Co., (a) U.S. pat. 1,709,315 (1929); (b) 1,790,622, 1,809,170 (1931); (c) 1,826,138, 1,826,139, 1,826,140, 1,826,141, 1,826,142, 1,826,143, 1,826,144, 1,826,145, 1,826,146, 1,826,147 (1931); (d) 1,890,516 (1932)—C.A. 23, 2820; 25, 1374, 4395; 26, 589; 27, 1745.
928. Arthur Lachman to Vapor Treating Processes, Inc., (a) U.S. pat. 2,035,607, 2,035,608 (1936); (b) 2,035,609 (1936); (c) 2,035,610 (1936); (d) 2,042,718 (1936)—C.A. 30, 3626, 3627, 5024.

929. H. N. LaCroix, *Natl. Petroleum News*, 33, No. 10, R-72-80 (1941); 36, No. 9, R 170-1 (1944); *World Petroleum*, 15, No. 3, 56-7 (1944)—C.A. 35, 3071; 38, 2814, 2191.
930. R. H. Laird, U.S. pat. 507,230 (1893).
931. H. A. Laitinen, A. S. O'Brien, and J. S. Nelson, *Anal. Chem.*, 18, 471-2 (1946)—C.A. 40, 5668.
932. G. R. Lake to Union Oil Co. of Calif., U.S. pat. 2,405,258 (1946)—C.A. 40, 6252.
933. W. A. LaLande, Jr., to Attapulgas Clay Co., U.S. pat. 2,451,564 (1948)—C.A. 44, 4666.
934. D. M. Lamb, U.S. pat. 183,401 (1876).
935. August Laurent, *J. prakt. Chem.*, 51, 242-3 (1850).
936. T. F. Lavine, *J. Biol. Chem.*, 109, 141-5 (1935); 113, 583-97 (1936)—C.A. 29, 4399; 30, 3842.
937. W. A. Lazier and J. V. Vaughen to Du Pont Co., U.S. pat. 2,041,840 (1936)—C.A. 30, 5006.
938. W. G. Leamon, (a) U.S. pat. 1,769,791, 1,769,795 (1930); (b) 1,769,792, 1,769,793, 1,769,794 (1930)—C.A. 24, 4625.
939. H. Z. Lecher, (a) *Ber.*, 48, 1425-32 (1915); (b) *ibid.*, 53, 568-77 (1920)—C.A. 9, 3241; 14, 3078.
- 939.5. H. Z. Lecher and Elizabeth M. Hardy, *J. Org. Chem.*, 20, 475-87 (1955)—C.A. 50, 4101.
940. H. Z. Lecher and Werner Siefkin, *Ber.*, 59, 1314-21, 2594-2601 (1926)—C.A. 20, 2976.
941. M. W. Lee to Union Oil Co. of Calif., (a) U.S. pat. 2,337,826 (1943); (b) 2,417,308 (1947)—C.A. 38, 3824; 41, 7104.
942. S. W. Lee and Gregg Dougherty, *J. Org. Chem.*, 4, 48-53 (1939)—C.A. 33, 4191.
943. T. W. Legatski and H. R. Legatski, *Oil Gas J.*, 45, No. 1, 99-707 (1946)—C.A. 40, 4504.
944. R. E. Lege, *Refiner Natural Gasoline Mfr.*, 16, 327-30 (1937)—C.A. 31, 8903.
945. P. C. Lemale, *Fr. pat.* 589,095 (1925)—C. 1925, II, 1239.
946. T. A. Lennartz and Rudolf Middeldorf, *Süddeut. Apoth. Ztg.*, 89, 593-5 (1949)—C.A. 44, 76.
947. W. B. Lerch, C. H. Mathis, and E. J. Gatchell to Phillips Petroleum Co., U.S. pat. 2,235,936 (1941)—C.A. 35, 4587.
948. R. Leuckart, *J. prakt. Chem.*, [2] 41, 179 (1890).
949. L. N. Leum to Atlantic Refg. Co., U.S. pat. 2,320,939 (1943)—C.A. 37, 6880.

950. L. N. Leum and E. R. Birkhimer to Atlantic Refg. Co., U.S. pat. 2,309,652, 2,309,653, 2,309,654 (1942)—C.A. 37, 4240.
951. P. A. Levene and L. A. Mikeska, *J. Biol. Chem.*, **70**, 365–80 (1926)—C.A. 21, 52.
952. Lewes, *The Carbonization of Coal*, (1912).
953. R. I. Lewis to Shell Dev. Co., (a) Can. pat. 290,441 (1929); (b) 318,892 (1932)—C. 1932, I, 3252; C.A. 26, 2048.
954. R. I. Lewis to N. V. de Bataafsche, Brit. pat. 345,596 (1929)—C.A. 26, 293.
955. Eugene Lieber and Raphael Rosen, U.S. pat. 1,976,806 (1934)—C.A., 28, 7441.
956. A. P. Lien, D. A. McCaulay, and B. L. Evering, *Ind. Eng. Chem.*, **41**, 2698–2702 (1949)—C.A. 44, 2214.
957. C. L. Lightenhome, U.S. pat. 1,434,300 (1922)—C.A. 17, 467.
958. Leon Lilienfeld, Ger. pat. 254,762 (1910)—C.A. 7, 1110.
959. W. B. Lindsay and W. B. Davidson, Brit. pat., 232,347 (1925)—C.A. 19, 3585.
960. R. Lindskog, *Svenska Gasfören, Månadsblad*, **14**, 26–8 (1947)—C.A. 42, 5210.
961. Louis Link and M. B. Amis to S. O. Dev. Co., U.S. pat. 1,718,714 (1929)—C.A. 23, 4059.
962. Arnold Lippert and E. E. Reid, *J. Am. Chem. Soc.*, **60**, 2370–1 (1938)—C.A. 33, 127.
963. H. K. Livingston, *Oil Gas J.*, **46**, No. 45, 80–7 (1948); *Ind. Eng. Chem.*, **41**, 888–93 (1949)—C.A. 42, 5650; 43, 5579.
964. H. K. Livingston, J. L. Hyde, and M. H. Campbell, *Ind. Eng. Chem.*, **41**, 2722–26 (1949)—C.A. 44, 2215.
965. Gustaf Ljunggren and Bo Norberg, *Acta Physiol. Scand.*, **5**, 248–55 (1943)—C.A. 38, 5970.
966. D. J. Loder to Du Pont Co., U.S. pat. 2,075,295 (1927)—C.A. 31, 3505.
967. O. Loew, U.S. pat. 101,284 (1870).
968. Carl Löwig, *Pogg. Ann.*, **47**, 153–61 (1839).
969. Carl Löwig and Salomon Weidmann, (a) *Pogg. Ann.*, **46**, 91; *ibid.*, **49**, 123 (1840); (b) *ibid.*, 323–40—*Ann.*, **36**, 321–23 (1840).
970. L. Logan and G. G. Desy, *Natural Gas*, **5**, No. 2, 12–3, 36–44 (1924)—C.A. 18, 1560.

971. W. B. Logan to The Texas Co., U.S. pat. 1,998,765 (1935)—C.A. 29, 3823.
972. J. L. Looney, U.S. pat. 1,777,005 (1930)—C.A. 24, 5999.
973. E. J. Lorand to Hercules Powder Co., U.S. pat. 2,395,055 (1946)—C.A. 40, 3007.
974. G. A. Lorenz to Shell Dev. Co., U.S. pat. 2,224,636 (1940)—C.A. 35, 2710.
975. C. Lossen, U.S. pat. 537,121 (1895).
976. L. L. Lovell and L. F. Boullion to Shell Dev. Co., U.S. pat. 2,293,395 (1942)—C.A. 37, 1260.
977. L. L. Lovell, P. E. Malson, and L. F. Boullion to Shell Dev. Co., U.S. pat. 2,306,993 (1942); Brit. pat. 560,225 (1944)—C.A. 37, 3920; 40, 1652.
978. L. L. Lovell, A. E. Martin, and F. W. Bell, to Shell Dev. Co., U.S. pat. 2,346,497 (1944)—C.A. 38, 5393.
979. W. H. Low to Richfield Oil Co. of Calif., U.S. pat. 1,777,619 (1930)—C.A. 24, 6001.
980. W. P. Lowe and C. W. Bilfinger, U.S. pat. 556,155 (1896).
981. C. D. Lowry, Jr., U. Oil Prods. Co. Booklet No. 242, 5-11 (1940)—C.A. 34, 8238.
982. C. D. Lowry, Jr. to U. O. Prods. Co., U.S. pat. 2,270,322 (1942)—C.A. 36, 3954.
983. C. D. Lowry, Jr., C. G. Dryer, Charles Wirth III, and R. E. Sutherland, Ind. Eng. Chem., 30, 1275-9 (1938)—C.A. 33, 845.
984. C. D. Lowry, Jr. and Gustav Egloff, Oil Gas J., 40, No. 31, 52-54 (1941)—C.A. 36, 2125.
985. C. D. Lowry, Jr. and F. C. Moriarty, Oil Gas J., 44, No. 26, 105-9 (1945)—C.A. 40, 701.
986. C. D. Lowry, Jr. and R. E. Sutherland to U. O. Prods. Co., U.S. pat. 2,336,109 (1943)—C.A. 38, 3824.
987. V. J. Loyd to Socony-Vac. Oil Co., U.S. pat. 2,315,530, 2,316,092 (1943)—C.A. 37, 5855.
988. H. A. Lubs and A. L. Fox to Du Pont Co., U.S. pat. 1,839,155 (1931)—C.A. 26, 1225.
989. C. C. Lucas and E. J. King, Biochem. J., 27, 2076-89 (1932)—C.A. 27, 3164.
990. O. D. Lucas and E. L. Lomax, U.S. pat. 1,615,286 (1927)—C.A. 21, 819.
991. O. D. Lucas, T. C. Palmer, and F. M. Perkin, Brit. pat. 108,019 (1916)—C.A. 11, 2961.
992. O. D. Lucas and V. L. Oil Processes Ltd., (a) Brit. pat. 214,871 (1923); (b) 219,403 (1923)—C.A. 18, 2804; 19, 726.

993. O. Lugo, U.S. pat. 60,757 (1867).
994. Lukaschewicz. *Z. f. Chemie*, 1868, 641.
995. G. Lunge, *Z. angew. Chem.*, 7, 69-74 (1894).
996. G. Lupton, U.S. pat. 110,054 (1870).
997. Martin Luther and Kurt Pieroh to I. G. Farben., U.S. pat. 1,732,371 (1929)—C.A. 24, 234.
998. W. A. Lutz and E. R. Butcher to Gulf Oil Co., U.S. pat. 2,303,853 (1942)—C.A. 37, 3263.
999. E. E. Lyder to S. O. Co. of Calif., U.S. pat. 2,208,591 (1940)—C.A. 35, 612.
1000. A. L. Lyman, R. C. Mithoff, and H. B. Nichols to S. O. of Calif., U.S. pat. 2,236,216 (1941)—C.A. 35, 4587.
1001. A. L. Lyman, H. B. Nichols, and R. C. Mithoff to S. O. Co. of Calif., U.S. pat. 2,143,078 (1939)—C.A. 33, 3128.
- 1001.5. J. P. Lyon, Jr., and A. A. Harban to Phillips Pet. Co., U.S. pat. 2,581,493 (1952)—C.A. 47, 143.
1002. C. F. Mabery, (a) *J. Franklin Inst.*, 139, 401-24 (1895); (b) *Am. Chem. J.*, 18, 43-79 (1896); *J. Soc. Chem. Ind.*, 19, 508 (1900).
1003. C. F. Mabery and J. Quayle, *J. Soc. Chem. Ind.*, 19, 505 (1899); *Proc. Am. Acad. Sci.*, 41, 87 (1905); *Am. Chem. J.*, 35, 404 (1906).
1004. A. M. McAfee, *Natl. Petroleum News*, (2) 7, 20-5 (1915); *Chem. Met. Eng.*, 13, 592-7 (1915); *Ind. Eng. Chem.*, 7, 737-41 (1915)—C.A. 9, 2147, 2812.
1005. A. M. McAfee, Brit. pat. 22,922 of 1914; U.S. pat. 1,277,092, 1,277,328, 1,277,329 (1918); 1,326,072 (1919)—C.A. 10, 1430; 12, 2126, 2125; 14, 1625.
1006. A. M. McAfee, (a) Can. pat. 163,092 (1915); (b) U.S. pat. 1,608,328 (1926); (c) 1,608,329 (1926)—C.A. 9, 2729; 21, 317.
- 1006.5. D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *J. Am. Chem. Soc.*, 73, 3627-32 (1951)—C.A. 46, 5519.
1007. T. Macalpine, (a) U.S. pat. 655,500 (1900); (b) 741,517 (1903).
1008. A. K. Macbeth and D. D. Pratt, *J. Chem. Soc.*, 119, 354-8 (1921)—C.A. 15, 1699.
1009. W. F. M. McCarty, U.S. pat. 1,274,912, 1,274,913 (1918)—C.A. 12, 2052.
1010. R. S. McClaughry and L. V. Moore to S. O. Co. of Ind., U.S. pat. 1,927,068 (1933)—C.A. 27, 5959.
1011. J. M. McClave to Conservo Co., U.S. pat. 1,703,158 (1929)—C.A. 23, 2029.

1012. J. H. McClintock to S. O. Dev. Co., U.S. pat. 2,324,790 (1943)—C.A. 38, 481.
1013. T. McClurkin, *Oil Colour Trades J.*, 95, 1078–80 (1939); *J. Inst. Petroleum*, 25, 382–9 (1939)—C.A. 33, 4668, 7921.
1014. E. B. McConnell to S. O. Co. of Ohio, U.S. pat. 2,148,869 (1939)—C.A. 33, 4419.
1015. T. F. McCormick to Tide Water Assoc. Oil Co., U.S. pat. 2,219,109 (1940)—C.A. 35, 1624.
1016. T. F. McCormick and Arthur Lazar to Tide Water Assoc. Oil Co., U.S. pat. 2,183,968 (1939)—C.A. 34, 2584.
1017. J. H. McCullough to Atlantic Refg. Co., U.S. pat. 2,269,467 (1942)—C.A. 36, 3351.
1018. J. H. McCullough, E. R. Birkhimer, and L. N. Leum to Atlantic Refg. Co., U.S. pat. 2,309,651 (1943)—C.A. 37, 4238.
1019. P. J. McDermott to Refiners, Ltd., U.S. pat. 1,999,335 (1935)—C.A. 29, 4165.
1020. Thomson McGowan, (a) U.S. pat. 257,961 (1882); (b) 292,419 (1893); (c) 658,857 (1900)—*J. Soc. Chem. Ind.*, I, 352 (1882).
1021. I. J. W. MacHattie and N. L. McNiven, *Can. Chem. Process Inds.*, 30, 87–90, 92, 94 (1946)—C.A. 40, 5546.
1022. Gordon McIntyre and E. G. Ulbricht to S. O. Dev. Co., U.S. pat. 1,985,613 (1945)—C.A. 29, 1241.
1023. H. C. McKee, L. K. Herndon, and J. R. Withrow, *Anal. Chem.*, 20, 301–3 (1948)—C.A. 42, 5214.
1024. D. S. McKittrick, *Ind. Eng. Chem.*, 21, 585–92 (1929)—C.A. 23, 3565.
1025. D. S. McKittrick to Shell Dev. Co., (a) U.S. pat. 2,114,852 (1938); (b) 2,204,903 (1940)—C.A. 32, 4772; 34, 7596.
1026. B. L. MacKusick and H. A. Alves, *Oil Gas J.*, 42, No. 49, 126, 127, 252, 255 (1944)—C.A. 38, 4416.
1027. Gordon MacLean to The Turbo-Mixer Corp., U.S. pat. 2,290,980 (1942)—C.A. 37, 556.
1028. P. McMichael, U.S. pat. 1,655,068 (1928)—C.A. 22, 1036.
1029. F. H. McMillan and J. A. King, *J. Am. Chem. Soc.*, 70, 4143–50 (1948)—C.A. 43, 2187.
1030. T. L. McNamara to Pure Oil Co., U.S. pat. 2,335,347 (1943)—C.A. 38, 3825.
1031. T. L. McNamara and L. M. Henderson to Pure Oil Co., U.S. pat. 2,316,965, 2,316,966 (1943)—C.A. 37, 6120.

1032. E. W. McNealy to The Texas Co., U.S. pat. 2,372,441 (1945)—C.A. 40, 454.
1033. R. W. McOmie, O. L. Davis, and A. C. Nixon to Shell Dev. Co., U.S. pat. 2,337,262 (1943)—C.A. 38, 3813.
1034. C. Märcker, *Ann.*, 136, 75–95 (1865).
1035. P. L. Magill to Roessler and Hasslacher Chem. Co., U.S. pat. 1,807,924 (1931); 1,890,881 (1932)—C.A. 25, 4394; 27, 1743.
1036. Hans Magnus, *Ger. pat.* 500,718 (1930)—C.A. 24, 4928.
1037. Alfonse, Mailhe and M. Murat, *Bull. soc. chim.*, [4] 7, 288–91 (1910)—C.A. 4, 2297.
1038. Boris Malishev, *Petroleum Z.*, 28, No. 17, 7–10 (1932)—C.A. 26, 4705.
1039. Boris Malishev to Shell Dev. Co., (a) *Can. pat.* 322,513 (1932); (b) U.S. pat. 1,914,953 (1933)—C.A. 26, 3659; 27, 4390.
1040. Boris Malishev, U.S. pat. 2,223,524 (1940)—C.A. 35, 2313.
1041. W. M. Malisoff to Atlantic Refg. Co., (a) *Can. pat.* 333,899 (1933); U.S. pat. 1,968,842 (1934); (b) 1,968,843 (1934); (c) 2,013,663 (1935); (d) 2,043,254 (1936)—C.A. 27, 4916; 28, 5975; 29, 7064; 30, 5403.
1042. W. M. Malisoff to Atlantic Refg. Co., (a) U.S. pat. 1,948,528 (1934); (b) 1,972,102 (1934); (c) 2,015,080 (1935)—C.A. 28, 2884, 6560; 29, 7635.
1043. W. M. Malisoff and C. E. Anding, Jr., *Anal. Chem.*, 7, 86–8 (1935)—C.A. 29, 3628.
1044. W. M. Malisoff and F. G. Hess to Atlantic Refg. Co., U.S. pat. 2,061,583 (1936)—C.A. 31, 846.
1045. W. M. Malisoff and E. M. Marks, (a) *J. Chem. Phys.*, 1, 284–5 (1933); *Ind. Eng. Chem.*, 23, 1114–20 (1931); (b) *ibid.*, 25, 780–3 (1933)—C.A. 27, 2866; 26, 82; 27, 4211.
1046. M. G. Mamedli, (a) *J. Applied Chem. (USSR)*, 18, 62–8 (1945); (b) *ibid.*, 20, 115–9 (1947)—C.A. 39, 5443; 41, 5705.
1047. W. Manchot and H. Gall, (a) *Ber.*, 60, 2318–22 (1927); 61, 2393–4 (1928); (b) *ibid.*, 62, 678–81 (1929)—C.A. 22, 2892; 23, 785, 4417.
1048. W. Manchot and F. Kaess, *Ber.*, 60, 2175–80 (1927)—C.A. 22, 199.
1049. M. R. Mandelbaum, *World Petr. Congr. London 1933*, Proc. 2, 21–9; *Petroleum World (London)*, 31, 44 (1934)—C.A. 28, 4878.

1050. M. R. Mandelbaum to Gray Processes Corp., U.S. pat. 1,965,105 (1934)—C.A. 28, 5657.
1051. Martin Maneck, Braunkohlenarch., No. 40, 53-90 (1933)—C.A. 27, 4907.
1052. R. E. Manley and H. H. Gross to The Texas Co., U.S. pat. 1,971,753 (1934)—C.A. 28, 6560.
1053. F. G. Mann and Donald Purdie, J. Chem. Soc., 1935, 1549-63—C.A. 30, 1680.
1054. G. L. Mann, Oil Gas J., 45, No. 46, 195-202 (1947)—C.A. 41, 4297.
1055. A. B. Manning, World Petr. Congr. London, 1933, Proc. 2, 7-9—C.A. 28, 4878.
1056. G. E. Mapstone, (a) Australian Chem. Inst. J. and Proc., 13, 156-60 (1946); (b) *ibid.*, 13, 232-8, 373-7 (1946); 15, 236-41 (1948); (c) *ibid.*, 13, 269-74 (1946); (d) *ibid.*, 14, 61-7 (1946)—C.A. 40, 4504, 7580; 41, 1176; 43, 7216; 40, 7578; 41, 4913.
1057. G. E. Mapstone, (a) Anal. Chem., 18, 498-9 (1946); (b) J. Inst. Petroleum, 34, 486-9 (1948); (c) *ibid.*, 35, 132-7 (1949)—C.A. 40, 6797; 42, 8455; 43, 4839.
1058. W. Marckwald, Ber., 33, 1556 (1900).
1059. Eugenio Mariani, Bull. sci. facolta chim. ind. Bologna, 3, 214-20 (1942)—C.A. 38, 5657.
1060. M. B. Markowitsch, Russ. pat. 23,515 (1931)—C.A. 26, 1769.
1061. A. M. Martin and L. Carlson, Oil Gas J., 40, No. 46, 138, 142-4 (1942)—C.A. 37, 518.
1062. A. R. Martin, P. J. Kelly, and K. H. Repath, U.S. pat. 1,858,635 (1932)—C.A. 26, 3913.
1063. Hoke Martin, Oil Gas J., 29, No. 47, 57-8 (1931); Natl. Petr. News, 23, No. 14, 32F-32H (1931)—C.A. 25, 3814.
1064. C. S. Marvel and C. D. Lewis, J. Polymer Sci., 3, 354-7 (1948)—C.A. 42, 6566.
1065. G. N. Maslyanskii, Doklady Akad. Nauk SSSR, 45, 25-8 (1944)—C.A. 39, 1283.
1066. G. N. Maslyanskii and E. I. Mezhebovskaya, J. Gen. Chem. (USSR), 16, 701-8 (1946)—C.A. 41, 1205.
1067. C. F. Mason, R. D. Bent, and J. H. McCullough, Proc. Am. Pet. Inst., 22nd Ann. Meeting, Sect. III, 22, 45-51 (1941); Oil Gas J., 40, No. 26, 114, 116, 119 (1941)—C.A. 36, 2396, 4699.
1068. A. A. M. Massenet, Ger. pat. 421,263 (1925)—C. 1926, I, 1088.

1069. Mathieson Alkali Works, Inc., New York, 1923 (Industrial Bulletin).
1070. M. P. Matuszak to Phillips Petroleum Co., U.S. pat. 2,399,496 (1946)—C.A. 40, 4209.
1071. Jean Maurin and René Pâris, (a) Compt. rend., 231, 1297-8 (1950); (b) J. chim. phys., 48, No. 9/10, Transferts électroniques en solns. et aux électrodes, C 30-6, C 37-41, discussion C 41 (1941)—C.A. 45, 4121; 46, 10011.
- 1071.5. E. B. Maxted, Brit. pat. 490,775 (1938)—C.A. 33, 1478.
1072. E. B. Maxted and H. C. Evans, J. Chem. Soc., 1937, 603-6, 1004-8; 1938, 455-8—C.A. 31, 4882, 7322; 32, 5288.
- 1072.5. E. B. Maxted and Arthur Marsden, J. Soc. Chem. Ind., 65, 51-2 (1946)—C.A. 40, 3868.
- 1072.7. E. B. Maxted and J. J. Priestley, Gas J., 247, 477-8, 481-2, 515-16, 556-7, 593 (1946)—C.A. 40, 3586.
1073. C. D. Maze, Brit. Pat. 263,381 (1926)—C.A. 22, 162.
1074. J. R. Meadow to Socony-Vac. Oil Co., U.S. pat. 2,403,013 (1946)—C.A. 40, 6502.
- 1074.5. J. R. Meadow and J. C. Cavagnol, J. Org. Chem., 17, 488-91 (1952)—C.A. 47, 1696.
1075. J. R. Meadow and W. A. Stover to Socony-Vac. Oil Co., U.S. pat. 2,434,623 (1948)—C.A. 42, 7028.
1076. H. H. Meier and O. H. Dawson to S. O. Dev. Co., U.S. pat. 1,843,578 (1932)—C.A. 26, 1768.
1077. J. V. Meigs and E. J. Ford, Refiner Natural Gasoline Mfr., 2, No. 5, 6-7 (1923)—C.A. 17, 2496.
1078. M. Meissner and H. W. Thompson, Trans. Faraday Soc., 34, 1238-9 (1938)—C.A. 33, 1598.
1079. E. F. Meitzner to Rohm and Haas Co., U.S. pat. 2,517,127 (1950)—C.A. 45, 1810.
1080. L. A. Mekler to U. O. Prods. Co., U.S. pat. 1,897,617 (1933)—C.A. 27, 2797.
1081. N. N. Mel'nikov, Uspekhi Khim, 5, 443-50 (1936)—C.A. 30, 5180.
1082. William Mendius, Refiner Nat. Gasoline Mfr., 11, 370 (1932)—C.A. 26, 4454.
1083. C. C. Mengel, Sr., U.S. pat. 452,578 (1891).
1084. R. C. Menzies, J. Chem. Soc., 121, 2787-93 (1922)—C.A. 17, 970.
1085. P. W. Merchant, U.S. pat. 1,875,088 (1932)—C.A. 26, 6117.
1086. J. Merrill, U.S. pat. 32,704 (1861).

1087. G. Merserau, U.S. pat. 1,224,485 (1917)—C.A. 11, 2025.
1088. C. W. Mertz, H. W. Cutcher, and J. A. McBride to Phillips Petroleum Co., U.S. pat. 2,558,221 (1951)—C.A. 46, 1024.
1089. H. E. Messmore to Phillips Petroleum Co., U.S. pat. 2,393,476 (1946)—C.A. 40, 2620.
1090. H. E. Messmore and J. M. Mason to Phillips Petroleum Co., U.S. pat. 2,378,092 (1945)—C.A. 39, 3658.
1091. A. Mestern, Brennstoff-Chem., 14, 225 (1933)—C.A. 27, 5154.
1092. F. L. Mevill, Brit. pat. 370,911 (1931)—C.A. 27, 2564.
1093. Ernst von Meyer and P. Fischer, J. prakt. Chem., [2] 82, 521–38 (1910)—C.A. 5, 1595.
1094. P. Meyer, J. Inst. Pet. Technol., 17, 621–9 (1931)—C.A. 26, 2308.
1095. Jaroslav Milbauer, Chem. Obzor, 12, 57–62 (1937)—C.A. 31, 6093.
1096. Christina C. Miller, J. Chem. Soc., 1941, 792; Analyst, 69, 109–12 (1944)—C.A. 36, 2228; 38, 3566.
1097. Ellis Miller, F. S. Crossley, and M. L. Moore, J. Am. Chem. Soc., 64, 2322–3 (1942)—C.A. 37, 99.
1098. E. B. Miller, U.S. pat. 1,647,459 (1927)—C.A. 22, 315.
1099. E. B. Miller and G. C. Connolly to Silica Gel Corp., Brit. pat. 280,947 (1926)—C.A. 22, 3519.
1100. L. P. Miller, Contrib. Boyce Thompson Inst., 3, 309–12 (1931); 5, 29–81 (1933)—C.A. 25, 5445; 27, 1914.
1101. L. P. Miller, J. D. Guthrie and F. E. Denny, Contrib. Boyce Thompson Inst., 8, 41–61 (1936)—C.A. 30, 6039.
1102. R. W. Miller to Pittsburgh Plate Glass Co., U.S. pat. 2,052,239 (1936)—C.A. 30, 7322.
1103. W. Miller to Continental Oil Co., U.S. pat. 2,041,364 (1936)—C.A. 30, 4660.
1104. A. Millschau, U.S. pat. 38,641 (1863).
1105. Minerals Separation, Ltd., Brit. pat. 549,975 (1942)—C.A. 38, 945.
1106. F. W. Minshall, U.S. pat. 415,876 (1889).
1107. Masakichi Mizuta, J. Soc. Chem. Ind. Japan, 34, Suppl. 287–8 (1931)—C.A. 25, 5976.
1108. Masakichi Mizuta and Teiji Yoshimura to Nippon Sekiyu Kabushiki Kaisha, U.S. pat. 2,080,087 (1937); 2,131,519 (1938); 2,154,988 (1939)—C.A. 31, 4804; 32, 9473; 33, 5644.
1109. B. L. Moldavskii and Z. I. Kumari, J. Gen. Chem. (USSR), 4, 298–306, 307–9 (1934)—C.A. 29, 1814.

1110. H. R. Moody, U.S. pat. 1,472,882 (1923)—C.A. 18, 465.
1111. C. C. Moore and W. L. Kent, S.A.E. Quart. Trans., 1, 687-93 (1947)—C.A. 42, 3943.
1112. G. H. Moore, U.S. pat. 586,520 (1897).
1113. Harold Moore and James Barrett, J. Inst. Petroleum Tech., 12, 582-5 (1926)—C.A. 21, 1703.
1114. William Moore, J. Agr. Research, 10, 365-71 (1917).
1115. William Moore and F. L. Campbell, J. Agr. Research, 28, 395-402 (1924)—C.A. 18, 3674.
1116. R. C. Moran to Vacuum Oil Co., U.S. pat. 1,692,756 (1928)—C.A. 23, 696.
1117. J. S. Morgan, U.S. pat. 1,536,908 (1925)—C.A. 19, 1919.
1118. Sergius Morgulis and D. E. Green, Protoplasma, 14, 161-9 (1931)—C.A. 26, 1037.
1119. F. C. Moriarty, Natl. Petroleum News, 36, R 163-9, R 307 (1944); Oil Gas J., March 30, (1944); Calif. Oil World, 37, No. 8, 19, 21, 23 (1944); Petroleum Engr., 15, No. 7, 150, 152 (1944); *ibid.*, 18, No. 5, 167-72 (1947); Petroleum World (Calif.), 41, No. 6, 53-5 (1944)—C.A. 38, 2814, 4783; 41, 2880.
1120. F. C. Moriarty to U. O. Prods. Co., U.S. pat. 2,348,745 (1944)—C.A. 39, 1046.
1121. J. C. Morrell, (a) Chem. Met. Eng., 30, 785-7 (1924); (b) Ind. Eng. Chem., 17, 101-2 (1925); (c) *ibid.*, 18, 733-8 (1926)—C.A. 19, 167, 1046; 20, 2742.
1122. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,568,904 (1926); 1,710,063 (1929); (b) 1,569,870, 1,569,871, 1,569,872 (1926); 1,949,756 (1934)—C.A. 20, 661; 23, 2819; 20, 817; 28, 2885.
1123. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,799,431 (1931); (b) 1,839,114 (1931); (c) 1,973,500 (1934); (d) 2,061,845 (1936)—C.A. 25, 3158; 26, 1429; 28, 6993; 31, 846.
1124. J. C. Morrell to U. O. Prods. Co., U.S. pat. 1,853,920, 1,853,921 (1932); 1,930,249, 1,935,162, 1,941,267 (1933); 1,950,739 (1934)—C.A. 26, 3370; 28, 312, 889, 1523, 3576.
1125. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,854,417 (1932); (b) 1,927,182 (1933); (c) 1,933,748 (1933); 2,009,898 (1935)—C.A. 26, 3370; 27, 5960; 28, 628; 29, 6416.
1126. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,904,381 (1933); (b) 1,904,382 (1933); (c) 1,911,640 (1933); (d) 2,002,747 (1935)—C.A. 27, 3600, 3601, 4067; 29, 4931.

1127. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,920,270 (1933); (b) 1,963,556 (1934); (c) 1,968,089 (1934); (d) 2,098,059 (1937)—C.A. 27, 4918; 28, 5224, 5975; 32, 344.
1128. J. C. Morrell to U. O. Prods. Co., (a) U.S. pat. 1,940,726 (1933); (b) 1,973,499 (1934); 1,988,083 (1935); (c) 2,034,197 (1936)—C.A. 28, 1520, 6993; 29, 1618; 30, 3220.
1129. J. C. Morrell and W. L. Benedict to U. O. Prods. Co., (a) U.S. pat. 2,197,873 (1940); (b) 2,289,924 (1942)—C.A. 34, 6060; 37, 759.
1130. J. C. Morrell, W. L. Benedict, and Gustav Egloff, Ind. Eng. Chem., 28, 122-8, 448-52 (1936)—C.A. 30, 2738, 3979.
1131. J. C. Morrell and D. J. Bergman, Chem. Met. Eng., 35, 350-4 (1928)—C.A. 22, 3038.
1132. J. C. Morrell and S. Comay, U.S. pat. 1,627,055 (1927)—C.A. 21, 2185.
1133. J. C. Morrell and Gustav Egloff, (a) Refiner Natural Gasoline Mfr., 2, No. 9, 5-10, 16-20, 36 (1923); (b) Oil Gas J., 32, No. 45, 51, 54-5, 57 (1934); (c) World Petroleum Congr., London, 1933, Proc. 2, 10-20—C.A. 28, 4579, 4878.
1134. J. C. Morrell and Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,946,096 (1934); (b) 1,947,868 (1934); (c) 1,947,869 (1934); (d) 1,979,565 (1934); 2,057,629, 2,057,630 (1936); (e) 2,087,525 (1937)—C.A. 28, 2517, 2888; 29, 334; 30, 8595; 31, 6452.
1135. J. C. Morrell and Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,855,486 (1932); (b) 1,897,582, 1,935,160, 1,935,161, 1,941,266 (1933); 1,946,094, 1,946,095 (1934)—C.A. 26, 3370; 27, 2797; 28, 889, 1523.
1136. J. C. Morrell and Gustav Egloff to U. O. Prods. Co., U.S. pat. 1,967,174 (1934); 2,063,518 (1936)—C.A. 28, 5975; 31, 846.
1137. J. C. Morrell and Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,954,487, 1,954,488 (1934); (b) 1,957,794 (1934); (c) 1,967,173 (1934); 2,021,739, 2,021,740 (1935)—C.A. 28, 3884, 4218, 5975; 30, 603.
1138. J. C. Morrell and Gustav Egloff to U. O. Prods. Co., (a) U.S. pat. 1,868,333 (1932); (b) 1,954,486 (1934); (c) 2,063,517 (1936)—C.A. 26, 5201; 28, 3884; 31, 846.
1139. J. C. Morrell and J. L. Essex to U. O. Prods. Co., U.S. pat. 1,890,229, 1,890,230 (1932)—C.A. 27, 1744.
1140. J. C. Morrell and W. F. Faragher, Ind. Eng. Chem., 19, 1045-9 (1927)—C.A. 21, 3450.

1141. C. S. Morris to Petrolite Corp. Ltd., U.S. pat. 2,366,545 (1945)—C.A. 39, 2398.
1142. A. A. Morton, U.S. pat. 2,064,558 (1936)—C.A. 31, 850.
1143. Maurice Morton and R. V. V. Nicholls, Can. J. Research, 25B, 159–82 (1947)—C.A. 41, 6758.
1144. A. J. Morway to S. O. Dev. Co., Can. pat. 358,686 (1936)—C.A. 30, 5783.
1145. F. R. Moser, Petroleum Z., 29, No. 7, 5–6 (1933)—C.A. 27, 3594.
1146. F. R. Moser to Shell Dev. Co., (a) U.S. pat. 2,031,972 (1936); (b) 2,186,425 (1940)—C.A. 30, 2745; 34, 3487.
1147. Carrie G. Moses and E. E. Reid, J. Am. Chem. Soc., 48, 776–7 (1926)—C.A. 20, 1217.
1148. F. G. Moses, R. W. Hess, and R. L. Perkins to Barrett Co., U.S. pat. 1,739,369 (1930); 1,904,460 (1933); Can. pat. 313,446 (1931)—C.A. 24, 814; 27, 3436; 25, 4510.
1149. Eugen Mossgraber, (a) Brit. pat. 368,882 (1930); (b) Swiss pat. 153,206 (1932)—C.A. 27, 2293; C. 1932, II, 2909.
1150. L. M. Mott, U.S. pat. 54,192 (1866).
1151. A. Y. Mottlau to S. O. Dev. Co., U.S. pat. 2,287,118 (1942)—C.A. 37, 254.
1152. H. C. Mougey, Ind. Eng. Chem., 20, 18–21 (1928)—C.A. 22, 1032.
1153. C. Moureu and C. Dufraisse, Compt. rend., 178, 1861–4 (1924); Chem. Rev., 3, 113–62 (1926); Chemistry & Industry, 42, 819–28 (1928).
1154. H. J. Moyer to S. O. Dev. Co., U.S. pat. 2,311,562 (1943)—C.A. 37, 4891.
1155. A. M. Muckenfuss to Du Pont Co., U.S. pat. 2,073,973 (1937)—C.A. 31, 3254.
1156. Eugen Mueller to Winthrop Chem. Co., U.S. pat. 2,111,151 (1938)—C.A. 32, 3557.
1157. H. Müller, Arch. Pharm., 200, 147 (1872)—C. 1872, 529.
1158. M. Müller, J. prakt. Chem., [2] 4, 39–41 (1871).
1159. F. B. Muhlenberg, U.S. pat. 1,750,420 (1930)—C.A. 24, 2283.
1160. J. C. Munday, U.S. pat. 1,942,532 (1934)—C.A. 28, 1810.
1161. E. A. Munyan, Am. Gas J., 131, 53–4 (1929); Gas Age Record, 64, 499–500, 510 (1929)—C.A. 24, 226, 1723.
1162. E. V. Murphree, C. W. Tyson, D. L. Campbell, and H. Z. Martin to S. O. Dev. Co., U.S. pat. 2,362,296 (1944)—C.A. 39, 2867.

1163. E. J. Murphy, *Gas Age*, 84, No. 11, 23-7 (1939); *Am. Gas J.*, 151, No. 6, 9-13, 41 (1940)—C.A. 34, 2158.
1164. R. C. Murray, *J. Chem. Soc.*, 1933, 739-40—C.A. 27, 4216.
1165. K. A. Musatov, *Novosti Tekhniki*, 1940, No. 10, 30-1—C.A. 34, 7589.
1166. K. A. Musatov and L. G. Krimova, *J. Applied Chem. (USSR)*, 13, No. 2, 227-34 (1940); *Foreign Petr. Tech.*, 9, 61-73 (1940)—C.A. 34, 8239; 35, 4188.
1167. K. A. Musatov and S. S. Nifontova, *Neftyanoe Khoz.*, 1940, No. 3, 28-32; *J. Applied Chem. (USSR)*, 13, No. 2, 235-43 (Ger. 243) (1940)—Translation: *Foreign Petr. Tech.*, 9, 220-33 (1941)—C.A. 34, 8239, 8231; 36, 256.
1168. E. Mylius, *Ber.*, 5, 978-9 (1872).
1169. F. Mylius and A. Mazzucchelli, *Z. anorg. Chem.*, 89, 1-38 (1914)—C.A. 9, 419.
1170. F. C. Nachod to Atlantic Refg. Co., U.S. pat. 2,422,982 (1948)—C.A. 42, 9157.
- 1170.5. Masao Nakazaki, *J. Inst. Polytech. Osaka City Univ., Ser. C*, 2, 23-4 (1951)—C.A. 46, 7067.
1171. S. S. Nametkin, V. G. Putsillo, and E. P. Shcheglova, *Bull. acad. sci. URSS, Classe sci. tech.*, 1943, No. 1/2, 10-22—C.A. 39, 2863.
1172. S. S. Nametkin, P. I. Sanin, S. V. Makover, and A. N. Tzuiba, *J. Applied Chem. (USSR)*, 6, 494-507 (1933); *Goryuchie Slantzui*, 4, No. 1, 44-50 (1934)—C.A. 28, 3571, 6557.
1173. S. S. Nametkin, P. I. Sanin, and E. F. Rudakova, *Khim. Tverdogo Topliva*, 4, 332-54 (1933)—C.A. 28, 6288.
1174. S. S. Nametkin, P. I. Sanin, and A. N. Tzuiba, *Goryuchie Slantzui*, 4, No. 2, 40-4 (1934)—C.A. 28, 6557.
1175. S. S. Nametkin and A. S. Sosnina, (a) *J. Applied Chem. (USSR)*, 7, 123-6 (1934); (b) *Doklady Akad. Nauk SSSR*, 63, 775-8 (1948)—C.A. 28, 7493; 43, 2759.
1176. A. H. Nathan and M. T. Bogert, *J. Am. Chem. Soc.*, 63, 2361-6 (1941)—C.A. 35, 7407.
1177. H. J. Neback to U. O. Prods. Co., U.S. pat. 2,329,930 (1943)—C.A. 38, 1352.
1178. I. E. Neifert, F. C. Cook, R. C. Roark, W. H. Tonkin, E. A. Back, and R. T. Cotton, *U.S. Dept. Agr. Bull.*, 1330, 40 p. (1925).
1179. C. A. Neilson, J. S. Hume, and B. H. Lincoln, *Anal. Chem.*, 14, 464-5 (1942)—C.A. 36, 4697.

1180. V. Nekrasov and N. N. Mel'nikov, *Ber.*, 62, 2091-4 (1929)—C.A. 24, 87.
1181. J. R. Neller and G. M. Vance to The Texas Co., U.S. pat. 1,672,621 (1928); *Can. pat.* 286,732 (1929)—C.A. 22, 2660.
1182. J. F. Nelson, *Iowa State Coll. J. Sci.*, 12, 145-7 (1937)—C.A. 32, 3756.
1183. M. Nencki and N. Sieber, *Sitzber. Akad. der Wissen.*, 98, 417-22 (1889).
1184. A. C. Nesfield, *Brit. pat.* 183,527 (1921); 196,680 (1922)—C.A. 17, 206, 3786.
1185. C. Neuberg and F. F. Nord, *Ber.*, 47, 2264-71 (1914)—C.A. 8, 3299.
1186. H. Neumann, U.S. pat. 1,545,440 (1925)—C.A. 19, 2741.
1187. R. Newall, U.S. pat. 53,656 (1866).
1188. E. W. S. Nicholson and A. K. Redcay to S. O. Dev. Co., U.S. pat. 2,409,690 (1946)—C.A. 41, 275.
1189. F. Niemann, (a) *Archiv. f. Hygiene*, 19, 117-25 (1893); (b) *ibid.*, 19, 126-35 (1893).
1190. P. S. Nisson to Gray Processes Corp., U.S. pat. 2,016,342 (1935)—C.A. 29, 8312.
1191. A. C. Nixon to Shell Dev. Co., (a) U.S. pat. 2,305,549 (1942); (b) 2,379,098 (1945)—C.A. 37, 3925; 40, 720.
1192. A. C. Nixon and O. L. Davis to Shell Dev. Co., U.S. pat. 2,305,550 (1942)—C.A. 37, 3924.
1193. A. C. Nixon and D. L. Yabroff to Shell Dev. Co., U.S. pat. 2,341,878 (1944); 2,411,105 (1946)—C.A. 38, 4792; 41, 1084.
1194. C. R. Noller and J. J. Gordon, *J. Am. Chem. Soc.*, 55, 1090-4 (1933)—C.A. 27, 1861.
1195. M. H. Norris, D. H. Falkner, and M. C. Price, *J. Chem. Soc.*, 121, 2161-8 (1922)—C.A. 17, 61.
1196. P. Nowak, *Petroleum Z.*, 29, No. 2, 1-7 (1933)—C.A. 27, 2290.
1197. D. B. Nutt and J. A. Altschuler, *Natl. Petr. News*, 29, No. 17, 67-70 (1937); *Refiner Natural Gasoline Mfr.*, 16, 214-16 (1937)—C.A. 31, 8903.
1198. N. V. Bataafsche, (a) *Dutch pat.* 22,257 (1930); *Brit. pat.* 335,394 (1928); (b) 332,944 (1929); 353,507 (1930); (c) *Jugosl. pat.* 7950 (1931)—C.A. 24, 5087; 25, 1364, 588; 26, 3659; C. 1932, II, 1568.
1199. N. V. Bataafsche, (a) *Brit. pat.* 481,642 (1938); (b) *Fr. pat.* 792,586 (1936); (c) 825,515 (1938); (d) 843,793 (1939)—C.A. 32, 6261; 30, 4311; 32, 6559; 34, 7596.

1200. N. V. Bataafsche, (a) Fr. pat. 795,596 (1936); (b) 811,-249 (1937); (c) 814,191 (1937); Brit. pat. 499,978 (1939)—C.A. 30, 6181; 32, 586, 761; 33, 5173.
1201. N. V. Bataafsche, (a) Brit. pat. 481,235 (1938); (b) 503,-645 (1939); (c) 505,732 (1939); Fr. pat. 864,153 (1941)—C.A. 32, 6665; 33, 7547, 7817; 42, 9157.
1202. N. V. Bataafsche, (a) Fr. pat. 842,536 (1939); (b) Brit. pat. 512,364 (1939); (c) 529,997 (1940); (d) 678,568 (1952)—C.A. 34, 6807, 7105; 35, 612; 36, 1482.
1203. N. V. Bataafsche, Fr. pat. 827,345 (1938); Ger. pat. 724,397 (1942); Dutch pat. 51,866 (1942); 54,433, 54,691 (1943); 62,284 (1949)—C.A. 32, 8126; 37, 6121; 41, 3612, 4166, 3951; 43, 4844.
1204. N. V. Bataafsche, (a) Fr. pat. 49,755 (1939); Dutch pat. 50,316 (1941); 51,939 (1942); (b) 53,316 (1942); (c) 63,042 (1949)—C.A. 36, 2564; 35, 7703; 41, 3613, 3951; 43, 6646.
1205. N. V. Bataafsche, (a) Fr. pat. 753,229 (1933); (b) 798,-062 (1936); (c) 813,951 (1937); (d) 825,576, 826,385 (1938); (e) 864,157 (1941)—C.A. 28, 890; 30, 7326; 32, 1085, 6851, 7713; 42, 9157.
- 1205.5. N. V. Bataafsche (S. A. Ballard, K. E. Furman and H. deV. Finch), Ger. pat. 812,072 (1951)—C.A. 47, 4371.
1206. N. V. Internat. Hydrogeneeringsoetooien Maatschappij, Brit. pat. 591,347 (1947)—C.A. 42, 752.
1207. E. M. Nygaard and O. M. Reiff to Socony-Vac. Oil Co., U.S. pat. 2,320,047 (1943)—C.A. 37, 6880.
1208. G. G. Oberfell to Phillips Petroleum Co., U.S. pat. 2,419,-029 (1947)—C.A. 41, 7104.
1209. G. G. Oberfell, A. M. Ballard, R. C. Alden, E. L. Utsinger and W. R. Lentz, U.S. pat. 1,574,507 (1926)—C.A. 20, 1514.
1210. A. Oberle, U.S. pat. 1,599,429 (1926)—C.A. 20, 3563.
1211. Joseph Obermeyer, Ber., 20, 2918-28 (1887).
1212. R. D. Obolentozev and M. I. Dement'eva, Compt. rend. acad. sci. URSS, 51, 621-3 (1946)—C.A. 41, 1416.
1213. L. L. Odom, U.S. pat. 1,604,235 (1926)—C.A. 21, 172.
1214. J. P. O'Donnell, Oil Gas J., 43, No. 8, 45-7 (1944)—C.A. 39, 4446.
1215. Oil Refining Improvements Co., Ltd., Ger. pat. 374,042 (1920)—C. 1923, IV, 305.
1216. Oil Refining Improvements Co. Ltd. and J. J. Hood, Brit. pat. 206,535 (1922)—C.A. 18, 1195.

1217. H. S. Olcott, *Science*, 96, 454 (1942)—C.A. 37, 2407.
1218. V. I. Olenskii, *Vsesoyuz. Nauch. Issledo-vatel. Inst. Tabach. i Makho-roch. Prom.*, No. 129, 43–51 (Eng. 51) (1936)—C.A. 32, 4710.
1219. J. F. Olin to Sharples Sol. Corp., U.S. pat. 2,237,625 (1941)—C.A. 35, 4393.
1220. J. F. Olin and T. E. Deger to Sharples Chemicals, Inc., U.S. pat. 2,349,191 (1944)—C.A. 39, 710.
1221. J. C. D. Oosterhout to The Texas Co., (a) U.S. pat. 1,982,120 (1934); (b) 2,439,670 (1948)—C.A. 29, 595; 42, 8462.
1222. Alfons Oppenheim, *J. prakt. Chem.*, 81, 307 (1860).
1223. Oranienburger Chem. Fab., *Fr. pat.* 671,912 (1929)—C. 1930, II, 856.
1224. Emil Ott to Hercules Powder Co., U.S. pat. 2,046,277 (1936)—C.A. 30, 5833.
1225. Emil Ott and E. E. Reid, (a) *Ind. Eng. Chem.*, 22, 878–81 (1930); (b) *ibid.*, 882–4; (c) *ibid.*, 884–6—C.A. 24, 4757, 4758.
1226. Robert Otto, (a) *Ann.*, 143, 100–17, 205–28 (1867); (b) *Ber.*, 10, 939–41 (1877); (c) *ibid.*, 13, 1289–90 (1880); (d) *ibid.*, 1290–2; (e) *ibid.*, 1283–9.
1227. Robert Otto and Adalbert Rössing, *Ber.*, 19, 3132–8 (1888).
1228. W. V. Overbaugh to The Texas Co., U.S. pat. 2,056,618 (1936)—C.A. 30, 8597.
1229. L. Palfray, S. Sabetay, and Denise Sontag, *Compt. rend.*, 194, 102–4 (1932)—C.A. 26, 1591.
1230. Pan American Petroleum Co., *Brit. pat.* 338,482, 338,483, 338,484 (1929)—C.A. 25, 2557.
1231. H. O. Parker, U.S. pat. 1,622,879, 1,627,338 (1927)—C.A. 21, 1703, 2185.
1232. J. H. Parker, U.S. pat. 958,820 (1910)—C.A. 4, 2371.
1233. R. W. Parker, *Petroleum Engr.*, 12, No. 10, 114, 116, 119, 120 (1941)—C.A. 35, 6420.
1234. D. C. Parman, F. C. Bishopp, E. W. Laake, F. C. Cook, and R. C. Roark, *U.S. Dept. Agr. Bull.*, 1472, 32 p. (1927).
1235. Parris, *Oil Gas J.*, 29, No. 42, 148 (1931).
1236. L. W. Parsons and S. P. Coleman, U.S. pat. 1,640,720 (1927)—C.A. 21, 3454.
1237. Henri Pascal, *Ile Cong. mondial petrole*, 2, Sect. 2, *Phys. chim., raffinage*, 329–33 (1937)—C.A. 33, 355.

1238. P. P. Patel, I. Sen-Gupta, and G. C. Chakravarti, *J. Indian Inst. Sci.*, **13A**, 73–84 (1930)—C.A. **24**, 4770.
1239. W. A. Patrick, Jr., (a) U.S. pat. 2,114,313, 2,114,314, 2,114,315 (1938); (b) Private communication—C.A. **32**, 4770, 4766.
1240. H. C. Paulsen to S. O. Dev. Co., (a) U.S. pat. 2,278,665 (1942); (b) 2,330,735 (1943); (c) 2,324,948 (1943); (d) 2,327,547 (1943); (e) 2,343,794 (1944)—C.A. **36**, 6005; **38**, 1633, 246, 1103, 3813.
1241. M. G. Paulus to S. O. Co. of Ind., U.S. pat. 1,628,423, 1,628,532 (1927); 1,716,973 (1929)—C.A. **21**, 2186; **23**, 3805.
1242. C. Pauly and Robert Otto, *Ber.* **9**, 1639–41 (1876).
1243. D. E. Payne and Vandever Vorhees to S. O. Co. of Ind., U.S. pat. 2,431,770 (1947)—C.A. **42**, 6107.
- 1243.5. W. A. Payne and W. E. Vail to Du Pont Co., U.S. pat. 2,618,660 (1952)—C.A. **47**, 9347.
1244. T. J. Pelouze and Auguste Cahours, *Compt. rend.*, **54**, 1242–3 (1862); **56**, 505 (1863)—*Ann.*, **127**, 190–99 (1863).
1245. H. L. Pelzer to Sinclair Refg. Co., U.S. pat. 1,770,287 (1930)—C.A. **24**, 4623.
1246. J. P. Penisten to U. O. Prods. Co., U.S. pat. 2,293,759 (1942)—C.A. **37**, 1259.
1247. A. Pepper, *Brit. pat.* 20,077 of 1913—C.A. **9**, 711.
1248. F. M. Perkin, (a) *Chem. Trade J.*, **50**, 251–2 (1917); (b) *J. Inst. Petroleum Tech.*, **3**, 227–42 (1917)—C.A. **11**, 2041, 3424.
1249. H. F. Perkins, U.S. pat. 1,541,274 (1925)—C.A. **19**, 2271.
1250. P. P. Perkins—Private communication.
1251. John Perl and Reinhardt Schuhmann to Union Oil Co. of Calif., U.S. pat. 1,935,725 (1933)—C.A. **28**, 887.
1252. R. M. Perrine, (a) U.S. pat. 389,898 (1888); (b) 419,347 (1890).
1253. J. M. Pertierra, *Anales soc. españ. fis. quim.*, **28**, 1435–50 (1930); *Chimie & industrie*, **26**, 9–14 (1931)—C.A. **25**, 2547, 5542.
1254. A. J. van Peski to Shell Dev. Co., U.S. pat. 2,019,772 (1935)—C.A. **30**, 606.
1255. A. G. Peterkin, Jr., to Atlantic Refg. Co., U.S. pat. 1,810,369 (1931)—C.A. **25**, 4697.
1256. G. S. Petrov, U.S. pat. 1,233,700 (1917)—C.A. **11**, 2609.
1257. Grigori Petrow, *Fr. pat.* 627,984 (1927)—C. **1928**, I, 455.
1258. E. F. Pevero to The Texas Co., U.S. pat. 2,015,038 (1935)—C.A. **29**, 7634.

1259. J. E. Pew and A. E. Buell, *Natl. Petroleum News*, 32, No. 40, R. 354-8 (1940)—C.A. 34, 8239.
1260. J. K. Pfoff and A. Kreutzer, *Z. angew. Chem.*, 36, 437-9 (1923).
1261. E. B. Phillips and J. G. Stafford, U.S. pat. 1,639,531 (1927)—C.A. 21, 3268.
1262. E. B. Phillips and J. G. Stafford to Gray Processes Corp., U.S. pat. 1,687,992 (1928)—C.A. 23, 273.
1263. E. B. Phillips and J. G. Stafford to Sinclair Refg. Co., U.S. pat. 1,774,611 (1930)—C.A. 24, 5146.
1264. F. C. Phillips, *Z. anorg. Chem.*, 6, 229-54 (1894).
1265. Ross Phillips and H. T. Clarke, *J. Am. Chem. Soc.*, 45, 1755-7 (1923)—C.A. 17, 3319.
1266. Phillips Petroleum Co., (a) Fr. pat. 830,031 (1938); (b) Brit. pat. 513,934 (1939); (c) 614,636 (1948)—C.A. 33, 369; 35, 3074; 43, 4003.
1267. Aime Pictet and I. Lerczynska, *Bull. soc. chim.*, [4] 19, 326-34 (1916); *Arch. sci. phys. nat.*, 44, 400-1 (1917)—C.A. 10, 3154; 13, 182.
1268. Mathias Pier, F. Ringer, and Walter Simon, U.S. pat. 1,932,186 (1933)—C.A. 28, 625.
1269. Mathias Pier and Walter Simon to Standard-I. G. Co., U.S. pat. 1,975,475 (1934)—C.A. 28, 7516.
1270. R. B. Pierce, *Natl. Petroleum News*, 22, No. 46, 121-30 (1930)—C.A. 25, 406.
1271. R. B. Pierce, W. F. Krausel, and J. M. Lawson, *Oil Gas J.*, 47, No. 22, 96-7 (1948)—C.A. 43, 1171.
1272. R. B. Pierce and A. W. Trusty, U.S. pat. 2,060,112 (1936)—C.A. 31, 535.
1273. Herman Pines to U. O. Prods. Co., U.S. pat. 1,937,914 (1933)—C.A. 28, 1180.
1274. C. S. Piper and R. S. Beckwith, *J. Soc. Chem. Ind.*, 67, 374-9 (1948)—C.A. 43, 2893.
1275. W. H. Pitt, (a) U.S. pat. 379,492 (1888); (b) 411,394 (1889).
1276. W. H. Pitt and van Fleck, *Ger. pat.*, 45,958 (1888).
1277. M. M. E. Plait, *Fr. pat.* 858,391 (1940)—C.A. 42, 3169.
1278. Plauson's (Parent Co.) Ltd., (a) *Brit. pat.* 193,071 (1921); (b) 202,422 (1922)—C.A. 17, 3417; 18, 465.
1279. Plauson's Forschungsinstitut, *Ger. pat.* 352,189 (1922)—C. 1922, IV, 285.
1280. O. L. Polly and A. C. Byrns to Union Oil Co. of Calif., U.S. pat. 2,347,432 (1944); 2,385,645 (1945)—C.A. 39, 606; 40, 455.

1281. O. L. Polly, A. C. Byrns, and W. E. Bradley, *Ind. Eng. Chem.*, **34**, 755-8 (1942)—C.A. **36**, 4698.
1282. D. J. Pompeo, C. J. Penther and K. E. Hallikainen, *Instruments*, **16**, 402-3, 440, 442, 444 (1943)—C.A. **37**, 5285.
1283. J. W. Poole, *Refiner*, **6**, No. 3, 96, 98, 100 (1927); *Oil Gas J.*, **25**, No. 41, 154-6 (1927)—C.A. **21**, 2787.
1284. Wilhelm Posth and Franz Besemann to I. G. Farben., U.S. pat. 1,788,204 (1931)—C.A. **25**, 809.
1285. I. Y. Postovskii, N. P. Bednyagina, and M. A. Mikhailova, *Doklady Akad. Nauk SSSR*, **44**, 403-6 (1944); *Compt. rend. acad. sci. URSS*, **44**, 375-7 (1944)—C.A. **39**, 1529, 5073.
1286. I. Y. Postovskii and V. G. Plyusnin, *Neftyanoe Khozyaistvo*, **19**, 561-4 (1930)—C.A. **25**, 3470.
1287. P. O. Powers to Newport Industries, U.S. pat. 1,926,648 (1933)—C.A. **27**, 5709.
1288. F. S. Pratt, A. F. Swain, and D. N. Eldred, *J. Econ. Entomol.*, **26**, 1031-41 (1933)—C.A. **28**, 5589.
1289. W. B. Price, U.S. pat. 522,028 (1894).
1290. W. B. Price and E. Dietz, U.S. pat. 1,349,294 (1920)—C.A. **14**, 3152.
1291. W. A. Proell and F. K. Ovitz to S. O. Co. of Ind., U.S. pat. 2,361,651 (1944)—C.A. **39**, 2643.
1292. W. A. Proell and B. H. Shoemaker to S. O. Co. of Ind., U.S. pat. 2,505,910 (1950)—C.A. **44**, 7342.
1293. C. F. Prutton to Lubri-Zol Corp., U.S. pat. 2,318,629 (1943)—C.A. **37**, 6449.
1294. C. F. Prutton and A. K. Smith, *Brit. pat.* 454,552 (1936)—C.A. **31**, 1607.
1295. Robert Pschorr, *Ger. pat.* 380,059 (1923)—C. **1923**, IV, 753.
1296. P. V. Puchkov, *Khim. Tverdogo Topliva*, **6**, 852-60 (1935); *Neftyanoe Khozyaistvo*, **18**, No. 6, 44-51 (1937)—C.A. **31**, 1593; **32**, 7705.
1297. P. V. Puchkov and A. F. Nikolaeva, *J. Applied Chem. (USSR)*, **10**, 327-35 (1937)—C.A. **31**, 4801.
1298. A. N. Pudovik and N. N. Kudryavtseva, *J. Gen. Chem. (USSR)*, **20**, 848-54 (1950)—C.A. **44**, 9338.
1299. E. T. Pummill to Socony-Vac. Oil Co., U.S. pat. 2,078,773 (1937); 2,114,354 (1938)—C.A. **31**, 4491; **32**, 4773.
1300. S. Quarfort, *Svenska Gasfören, Manadsblad*, **1947**, No. 5, 85; *Dept. Sci. Ind. Research (Brit.) Fuel Abs.*, **2**, No. 5, 36 (1947)—C.A. **42**, 5204.

1301. G. G. Quinn, *Oil Gas J.*, 27, No. 44, 132, 139 (1929)—C.A. 23, 3336.
1302. T. Rabek, *Brennstoff-Chem.*, 11, 189-92 (1930)—C.A. 25, 187.
1303. E. V. Rakovskii and K. I. Suiskov, *Khim. Tverdogo Topliva*, 5, 161-75 (1934)—C.A. 28, 6290.
1304. A. S. Ramage, U.S. pat. 1,409,404 (1922)—C.A. 16, 1858.
1305. A. S. Ramage to Gyro Process Corp. (a) U.S. pat., 1,771,350 (1930); (b) *ibid.*, 1,796,621 (1931)—C.A. 24, 4624; 25, 2557.
1306. J. B. Rather, U.S. pat. 1,580,531 (1926)—C.A. 20, 1903.
1307. J. B. Rather and F. S. Shepard, U.S. pat. 1,622,671 (1927)—C.A. 21, 1703.
1308. B. Rathke, *Ann.*, 161, 148 (1872).
1309. F. E. Raurich Sas, *Anales soc. espan. fis. quim.*, 34, 419-94 (1936)—C.A. 30, 5900.
1310. P. A. Ray to Hercules Powder Co., U.S. pat. 2,073,492 (1937)—C.A. 31, 2874.
1311. P. C. Ray, (a) *J. Chem. Soc.*, 109, 131-8, 603-12 (1916); *ibid.*, 111, 101-9 (1917); (b) *ibid.*, 115, 548-52 (1919); (c) *ibid.*, 871-8; (d) *ibid.*, 123, 133-41 (1923)—C.A. 10, 1325, 2582; 11, 1422; 13, 2021, 2858.
1312. P. C. Ray, K. C. Bose-Ray, and N. B. Adhikari, *Quart. J. Indian Chem. Soc.*, 4, 467-75 (1928)—C.A. 22, 1922.
1313. P. C. Ray and Radhakishen Das, *J. Chem. Soc.*, 121, 323-8 (1922)—C.A. 16, 1953.
1314. P. C. Ray and P. C. Guha, *J. Chem. Soc.*, 115, 261-71, 541-8 (1919)—C.A. 13, 1707, 2021.
1315. C. L. Read and T. J. Broidrick to S. O. Dev. Co., U.S. pat. 2,146,027 (1939)—C.A. 33, 3581.
1316. Davis Read, Jr., *Petroleum Engr.*, 18, No. 3, 106-14 (1946)—C.A. 41, 1415.
1317. Davis Read, Jr., and W. L. Benedict to U. O. Prods. Co., U.S. pat. 2,298,411 (1942)—C.A. 37, 1859.
1318. Davis Read, Jr., and Gustav Egloff, *J. Inst. Petroleum*, 33, 621-7 (1947)—C.A. 42, 3159-61.
1319. E. H. Records and J. E. Louttit, U.S. pat. 2,232,971 (1941)—C.A. 35, 4192.
1320. Redwood, *Petr.*, 2, 383 (1906).
1321. B. Redwood, *Treatise on Petroleum*, Vol. 2, 515; London, Chas. Griffen & Co., 1922.
1322. R. M. Reed, *Oil Gas J.*, 45, No. 1, 99-107 (1946)—C.A. 40, 4504.

1323. W. W. Reed to Socony-Vac. Oil Co., U.S. pat. 2,306,843 (1942)—C.A. 37, 3925.
1324. H. V. Rees and C. F. Teichmann, U.S. pat. 1,955,607 (1934)—C.A. 28, 3883.
1325. Hans Reichard, Braunkohle, 26, 780-2 (1927)—C.A. 22, 494.
1326. E. E. Reid, C. M. Mackall, and G. E. Miller, J. Am. Chem. Soc., 43, 2104-7 (1921)—C.A. 16, 256.
1327. G. W. Reid, Oil Gas J., 24, No. 3, 119, 130, 132-3 (1925)—C.A. 19, 2559.
1328. J. A. Reid and W. A. Schulze to Phillips Petroleum Co., U.S. pat. 2,058,720 (1936)—C.A. 31, 247.
1329. Hans Reihlen and Adolf von Friedolsheim, Ann., 457, 71-82 (1927)—C.A. 22, 1134.
1330. Hans Reihlen, Adolph von Friedolsheim and Walter Oswald, Ann., 465, 72-96 (1928)—C.A. 22, 4476.
1331. S. P. Reimann, Protoplasma, 10, 82-3 (1930); Am. J. Cancer, 15, 2149-68 (1931); Arch. Pathol., 15, 675-97 (1933)—C.A. 25, 3725; 26, 1657; 27, 3985.
1332. S. P. Reimann and Nevart Chatalbash, Growth, 1, 247-9 (1937)—C.A. 32, 4667.
1333. S. P. Reimann and E. M. Hall, Arch. Pathol., 22, 55-61 (1936)—C.A. 30, 6440.
1334. S. P. Reimann and F. S. Hammett, Proc. Soc. Exptl. Biol. Med., 27, 20-2 (1929)—C.A. 24, 5310.
1335. S. P. Reimann and E. R. Hankele, Arch. Pathol., 17, 764-8 (1934)—C.A. 28, 5874.
1336. S. P. Reimann and Gerrit Toennies, Arch. Pathol., 29, 175-81 (1940)—C.A. 34, 2464.
1337. Herman Reinbold, U.S. pat. 1,600,845 (1926)—C.A. 20, 3563.
1338. Herman Reinbold and Hugo Reinbold, (a) U.S. pat. 1,558,631 (1925); (b) 1,558, 632 (1925); (c) 1,570,005 (1926)—C.A. 20, 108, 817.
1339. J. F. Reith, Rec. trav. chim., 53, 18-23 (1934)—C.A. 28, 1955.
1340. F. G. P. Remfry and A. E. Dunstan, (a) Brit. pat. 236,263 (1924); (b) 246,937 (1924)—C.A. 20, 974; B.A. 1926, 352B.
1341. T. R. Remy to The Texas Co., U.S. pat. 2,045,925 (1936)—C.A. 30, 5716.
1342. R. R. Renshaw, P. E. Dreisbach, M. Ziff, and D. Green, J. Am. Chem. Soc., 60, 1765-70 (1938)—C.A. 32, 7412.

1343. Report of the Institution of Gas Engineers' Committee of Inquiry, *Gas World*, 117, 435-8 (1942)—C.A. 37, 249.
1344. T. Restieaux, U.S. pat. 63,749 (1867).
1345. E. R. P. E. Retailiau and J. B. Wyman to Shell Dev. Co., U.S. pat. 2,126,503 (1938)—C.A. 32, 8128.
1346. A. Reyckler, *Bull. soc. chim. Belg.*, 27, 110-3 (1913)—C.A. 8, 1105.
1347. S. Reymann, *Ber.*, 7, 1287-90 (1874).
1348. Heinrich Rheinboldt, *Ber.*, 60, 184-6 (1927)—C.A. 21, 1626.
1349. Heinrich Rheinboldt, Friedrich Mott, and Erwin Motzkus, *J. prakt. Chem.*, [2] 134, 257-81 (1932)—C.A. 26, 5544.
1350. C. H. Richardson and C. R. Smith, *J. Agr. Research*, 33, 597-609 (1926)—C.A. 21, 472.
1351. M. Riche and M. Roume, *Annales des mines*, 184, 67-130 (1894).
1352. A. Richter and W. Schaefer, U.S. pat. 1,814,410 (1931)—C.A. 25, 5281.
1353. F. Richter, U.S. pat. 1,066,322 (1913)—C.A. 7, 3042.
1354. D. Rider, U.S. pat. 1,685,034 (1928)—C.A. 22, 4779.
1355. H. M. Ridge and W. R. Hodgkinson, *Brit. pat.* 203,354 (1922); U.S. pat. 1,608,339 (1926)—*J. Soc. Chem. Ind.*, 42, 1118A (1923); C.A. 21, 317.
1356. C. M. Ridgway, *Oil Gas J.*, 36, No. 46, 83-4, 88, 92, 94 (1938)—C.A. 32, 7707.
1357. C. M. Ridgway to Pure Oil Co., U.S. pat. 2,057,918 (1936)—C.A. 31, 247.
- 1357.5. C. H. Riesz, H. A. Dirksen, and W. J. Kirkpatrick, *Inst. Gas Technol. Research Bull.*, No. 10, 23 p. (1951)—C.A. 46, 2780.
1358. C. H. Riesz and Cornel Wohlberg, *Am. Gas Assoc. Proc.*, 25, 259-70 (1943)—C.A. 38, 4406.
1359. J. J. Ritter and Eva D. Sharpe, *J. Am. Chem. Soc.*, 59, 2351-2 (1937)—C.A. 32, 535.
1360. R. C. Roark and R. T. Cotton, U.S. Dept. Agr. Tech. Bull., 162, 52 p. (1930)—C.A. 24, 3595.
1361. G. Roberti, E. Pipparelli, and E. Sommariva, *Ann. chim. applicata*, 33, 67-71 (1943)—C.A. 39, 178; 40, 7580.
1362. C. I. Robinson to S. O. Co. of N. J., (a) U.S. pat. 910,569, 910, 584 (1909); 968,692 (1910); (b) 1,018,374 (1912)—C.A. 3, 1081; 4, 3003; 6, 930.
1363. P. M. Robinson, *Natl. Petroleum News*, 32, No. 34, R-298-304 (1940)—C.A. 34, 8238.

1364. P. J. Roelfsema to Shell Dev. Co., U.S. pat. 2,069,329 (1937)—C.A. 31, 1996.
1365. H. Roemer, Ber., 6, 784 (1873).
1366. F. M. Rogers to S. O. Co., Can. pat. 309,099 (1931)—C.A. 25, 1983.
1367. F. M. Rogers to S. O. Co. of Ind., U.S. pat. 2,007,146 (1935)—C.A. 29, 5645.
1368. T. H. Rogers and B. H. Shoemaker to S. O. Co. of Ind., U.S. pat. 2,164,665 (1939)—C.A. 33, 8395.
1369. F. Rohart, Ger. pat. 14,924 (1881).
- 1369.5. E. Rohrbaech, Ann., 315, 9–18 (1901).
1370. A. Romvalter, Roy. Hung. Palatine-Joseph Univ. Tech. Econ. Sci. Pubs. Dept., Mining Met., 14, 40–71 (1942)—C.A. 41, 7714.
1371. T. W. Rosebaugh to Shell Dev. Co., (a) Can. pat. 375,218 (1938); U.S. pat. 2,146,353 (1939); (b) 2,299,426 (1942)—C.A. 32, 7055; 33, 3579; 37, 2561.
1372. Raphael Rösen to Standard Catalytic Co., U.S. pat. 2,253,308 (1941)—C.A. 36, 258.
1373. Sheldon Rosenberg, J. C. Perrone, and P. L. Kirk, Anal. Chem., 22, 1186–7 (1950)—C.A. 45, 4168.
1374. Fritz Rosendahl, Petroleum Z., 28, No. 41, Motorenbetrieb u. Maschinen-Schmierung, 5, No. 10, 5–6 (1932)—C.A. 27, 180.
1375. Ludwig Rosenstein, U.S. pat. 1,943,744 (1934)—C.A. 28, 2175.
1376. Ludwig Rosenstein to Shell Dev. Co., (a) U.S. pat. 1,974,724, 1,974,725 (1934); (b) 2,110,403 (1938)—C.A. 28, 7516; 32, 3598.
1377. Ludwig Rosenstein and W. J. Hund, U.S. pat. 1,835,184 (1931)—C.A. 26, 1113.
- 1377.5. R. H. Rosenwald, Petroleum Processing, 6, 969–73 (1951)—C.A. 46, 1238.
1378. R. Ross and J. Race, J. Soc. Chem. Ind., 29, 604–8 (1910)—C.A. 4, 2365.
1379. Heliodor Rostin, (a) Fr. pat. 714,825 (1931); (b) U.S. pat. 1,451,052 (1923); (c) 1,904,172 (1933)—C.A. 26, 1768; 17, 2048; 27, 3325.
1380. Heliodor Rostin and Karl Schuster, U.S. pat. 2,171,009 (1939)—C.A. 34, 252.
1381. G. C. Rowden, U.S. pat. 1,845,723 (1932)—C.A. 26, 2311.
1382. G. L. Rowsey, Natl. Petroleum News, 18, No. 29, 18 (1926); U.S. pat. 1,754,649 (1930); 1,954,103 (1934)—C.A. 24, 2876; 28, 3888.

1383. G. L. Rowsey and J. F. Whitehurst, *Oil Gas J.*, 26, No. 32, 250-4 (1927)—C.A. 22, 1464.
1384. L. W. Royer to Skelly Oil Co., U.S. pat. 2,379,654 (1945)—C.A. 39, 3923.
1385. M. Rubner, *Archiv. f. Hygiene*, 19, 136-93 (1893).
- 1385.5. M. G. Rudenko and V. N. Gromova, *Doklady Akad. Nauk SSSR*, 81, 207-9 (1951)—C.A. 46, 7515.
1386. H. P. Rue, *Oil Gas J.*, 26, No. 51, 162 (1928); *Refiner Natural Gasoline Mfr.*, 7, No. 5, 62-3 (1928); U.S. Bur. Mines, *Repts. of Investigations*, No. 2862, 5 p. (1928)—C.A. 22, 2262.
1387. H. P. Rue and R. H. Espach, U.S. Bur. Mines, *Bull.* 333, 111 p. (1930)—C.A. 25, 1663.
- 1387.5. W. H. C. Rueggeberg, Private Communication.
1388. T. Ruemele, *Seifensieder Ztg.*, 66, 434-5 (1939)—C.A. 33, 5996.
1389. Rütgers-Werke A. G., Ger. pat. 153,585 (1904)—C. 1904, II, 800.
- 1389.5. C. L. Ruiz, L. L. Silva, and L. Libenson, *Rev. soc. Argentina biol.*, 6, 134-41 (1930); *Compt. rend. soc. biol.*, 104, 1029 (1930)—C.A. 25, 3079, 4058.
1390. A. L. Rummelsburg to Hercules Powder Co., U.S. pat. 2,329,486 (1943)—C.A. 38, 1053.
1391. W. H. Rupp and F. C. Hanker, Jr., to S. O. Dev. Co., U.S. pat. 2,341,389 (1944)—C.A. 38, 4792.
1392. J. T. Rutherford, (a) *Gas Age*, 87, 24 (1941); (b) *Proc. Am. Pet. Inst., Sect. IV*, 21, 89-91 (1940)—C.A. 35, 4180.
1393. R. F. Ruthruff to S. O. Co. of Ind., U.S. pat. 1,938,672 (1933)—C.A. 28, 1520.
1394. D. E. Ryan, *Anal. Chem.*, 22, 599-600 (1950)—C.A. 44, 6764.
1395. J. C. Ryan, *Ind. Eng. Chem.*, 34, 824-32 (1942); *Natl. Petroleum News*, 34, No. 30, R 234-9 (1942)—C.A. 36, 5987.
1396. L. R. Rykhan and C. L. A. Schmidt, *Univ. Calif. Pub. Physiol.*, 8, 257-76 (1944)—C.A. 38, 2977.
1397. Paul Sabatier and Alfonse Mailhe, *Compt. rend.*, 150, 1569-72 (1910)—C.A. 4, 2935.
1398. L. Sabrou and M. Renaudie, *Compt. rend. 17me Congr. chim. ind., Paris, Sept.-Oct., 1937*, 98-104—C.A. 32, 6437.
1399. A. P. Sachs to Petroleum Conversion Corp., U.S. pat. 2,191,043 (1940)—C.A. 34, 4895.
1400. Georg Sachs, *Z. anorg. allgem. Chem.*, 135, 273-82, 283-8 (1924); *Ber.*, 54, 1849-51 (1921)—C.A. 18, 3154; 16, 905.

1401. Georg Sachs and L. Balassa, *Z. anorg. Chem.*, **146**, 196–9 (1925)—C.A. **19**, 3069.
- 1401.5. Georg Sachs and Minna Ott, *Ber.*, **59**, 171–5 (1926)—C.A. **20**, 1605.
1402. Georg Sachs, L. Schlesinger, and H. Antoine, *Ann.*, **433**, 154–63 (1923)—C.A. **18**, 57.
1403. F. Sager, *Inst. Petroleum Tech.*, **22**, 609–15 (1936); *Refiner Natural Gasoline Mfr.*, **16**, No. 6, 298–304 (1939)—C.A. **30**, 8586; **31**, 8899.
1404. Baldassarre Saladini, (a) *Ann. chim. applicata*, **18**, 337–52 (1928); (b) *Industria chimica*, **4**, 1023–38 (1929); (c) *ibid.*, **4**, 1132–7 (1929); **5**, 1482–7 (1930); *Atti III Congresso Nazionale chim. pura applicata Firenze e Toscana, 1929*, 584 (1930)—C.A. **23**, 954; **24**, 1963, 2279; **25**, 2552, 2276.
1405. J. R. Sampey and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 3404–9 (1932)—C.A. **26**, 5034.
1406. G. E. Sample and W. B. Miller to Shell Dev. Co., U.S. pat. 2,434,868 (1948)—C.A. **42**, 7029.
1407. W. L. Savell, U.S. pat. 1,945,121 (1934)—C.A. **28**, 2515.
1408. R. R. Sayers, A. C. Fieldner, W. P. Yant, R. D. Leitch and S. J. Pearce, U.S. Bur. Mines Rept. of Investigations, **3007**, 13 p. (1930)—C.A. **24**, 3884.
1409. Alexander Saytzeff and N. Grabowsky, *Ann.*, **175**, 344–8 (1875).
1410. E. T. Scafe, *Petroleum Refiner*, **25**, No. 9, 413–8 (1946)—C.A. **42**, 9141.
1411. R. E. Schaad, U.S. pat. 1,954,843 (1934)—C.A. **28**, 3887.
1412. J. G. Schaafsma to Socony-Vac. Oil Co., U.S. pat. 2,364,390 (1944)—C.A. **39**, 3923.
1413. R. Schenck, *Z. anorg. allgem. Chem.*, **148**, 351–68 (1925)—C.A. **20**, 692.
1414. C. T. Schieman, Jr., *Petroleum Engr.*, **18**, 184–90 (1947)—C.A. **41**, 4913.
1415. M. Schiller, U.S. pat. 580,652 (1897).
1416. R. Schiller and Robert Otto, *Ber.*, **9**, 1638 (1876).
1417. Hans Schindler to Pure Oil Co., (a) U.S. pat. 2,367,803 (1945); (b) 2,405,905 (1946); (c) 2,488,479 (1949)—C.A. **39**, 3912; **40**, 6806; **44**, 2025.
1418. Hans Schindler, G. W. Ayres, and L. M. Henderson, *Anal. Chem.*, **13**, 326–8 (1941)—C.A. **35**, 4943.
1419. Paul Schlack to Alien Property Custodian, U.S. pat. 2,325,552 (1943)—C.A. **38**, 432.

1420. H. Schlosstein, U.S. pat. 1,638,643, 1,638,644 (1927)—C.A. 21, 3268.
1421. Hans Schmalfuss, *Fermentforschung*, 8, 1-41 (1924)—C.A. 18, 3388.
1422. Frithjof Schmeling, (a) *Braunkohlenarch.*, No. 45, 15-34 (1936); (b) *Oel, Kohle, Erdoel, Teer*, 12, 837-40 (1936)—C.A. 30, 7310; 31, 2398.
1423. A. T. Schmidt, U.S. pat. 164,694 (1875).
1424. H. Schmidt, *Petroleum Z.*, 23, 646-8 (1927)—C.A. 21, 2785.
1425. R. Schmitt and O. Mittenzwey, *J. prakt. Chem.*, [2] 18, 192-5 (1879).
1426. P. M. E. Schmitz, *Erdöl u. Teer*, 6, 493-4, 510-2 (1930); *Chimie & industrie*, Spec. No. 355-68 (1931)—C.A. 25, 2276, 3474.
1427. P. M. E. Schmitz, Belg. pat. 369,809 (1930); Fr. pat. 707,335 (1930)—C.A. 25, 810; 26, 838.
1428. K. Schneider and H. Feichtinger, *Angew. Chem.*, B20, 12-16 (1948)—C.A. 42, 7968.
1429. Wilhelm Schneider and August Bansa, *Ber.*, 64, 1321-4 (1931)—C.A. 25, 4232.
1430. Alfons Schöberl, (a) *Z. physiol. Chem.*, 201, 167-90 (1931); (b) *Ber.*, 70, 1186-93 (1937)—C.A. 26, 364; 31, 5762.
1431. J. R. Schonberg to S. O. Dev. Co., U.S. pat. 2,344,418 (1944)—C.A. 38, 3824.
1432. F. Schulze, *Petroleum Z.*, 5, 205, 446 (1909)—C.A. 4, 1365.
1433. W. A. Schulze to Phillips Petroleum Co., (a) U.S. pat. 1,998,849 (1935); (b) 2,151,721 (1939); (c) 2,206,921 (1940)—C.A. 29, 4163; 33, 5168; 34, 8255.
1434. W. A. Schulze to Phillips Petroleum Co., U.S. pat. 2,087,048 (1937); 2,162,319 (1939); 2,232,736, 2,234,505 (1941); 2,273,224, 2,291,581 (1942); 2,351,154 (1944)—C.A. 31, 6453; 33, 5168; 7551; 35, 4192; 36, 4324; 37, 1255; 38, 6084.
1435. W. A. Schulze to Phillips Petroleum Co., U.S. pat. 2,081,309 (1937); 2,131,525, 2,163,312 (1938); 2,204,234 (1940); 2,255,394, 2,264,220 (1941)—C.A. 31, 5144; 32, 9472; 33, 8000; 34, 7596; 36, 648, 2130.
1436. W. A. Schulze and R. C. Alden, Refiner, *Nat. Gasoline Mfr.*, 18, 474-7, 515; *Oil Gas J.*, 38, No. 27, 199, 200, 202-4 (1939)—C.A. 34, 1468.

1437. W. A. Schulze and A. E. Buell, *Natl. Petroleum News*, 27, No. 41, 25-6, 28, 30-1 (1935); *ibid.*, 29, No. 23, 54-9 (1937); *Oil Gas J.*, 34, No. 21, 22-4 (1935); *ibid.*, 36, No. 4, 59-65 (1937)—C.A. 29, 8306; 31, 5556; 30, 838; 32, 336.
1438. W. A. Schulze and A. E. Buell, (a) *Oil Gas J.*, 34, No. 22, 42-6 (1935); (b) *ibid.*, 36, No. 28, 56-7, 59 (1937); *Refiner Natural Gasoline Mfr.*, 16, No. 6, 268-71, 276 (1937)—C.A. 30, 1216; 32, 2723, 336.
1439. W. A. Schulze and A. E. Buell to Phillips Petroleum Co., U.S. pat. 2,315,820 (1943)—C.A. 37, 5856.
1440. W. A. Schulze and L. V. Chaney, *Natl. Petroleum News*, 25, No. 34, 37-8, 40 (1933)—C.A. 27, 5952.
1441. W. A. Schulze and L. V. Chaney to Phillips Petroleum Co., (a) U.S. pat. 2,022,942 (1935); 2,028,998 (1936); (b) 2,034,837 (1936)—C.A. 30, 847, 1987, 3219.
1442. W. A. Schulze and F. E. Frey to Phillips Petroleum Co., (a) U.S. pat. 1,964,219, 1,964,220 (1934); (b) 1,980,555 (1934)—C.A. 28, 5224; 29, 332.
1443. W. A. Schulze and L. S. Gregory, *Natl. Petroleum News*, 28, No. 41, 34-40, 75 (1936)—C.A. 31, 2405.
1444. W. A. Schulze and J. P. Lyon, Jr., to Phillips Petroleum Co., U.S. pat. 2,517,934 (1950)—C.A. 45, 638.
1445. W. A. Schulze and L. C. Morris to Phillips Petroleum Co., (a) U.S. pat. 2,271,665 (1942); 2,362,219 (1944); (b) 2,315,875 (1943)—C.A. 36, 3954; 39, 3154; 37, 5856.
1446. W. A. Schulze and G. H. Short to Phillips Petroleum Co., U.S. pat. 2,222,122 (1940); 2,242,621, 2,242,625 (1941)—C.A. 35, 1981, 6104.
1447. W. A. Schulze, V. W. Wilson, and A. E. Buell, *Oil Gas J.*, 37, 76 (1939)—C.A. 33, 8969.
1448. Fritz Schuster, *Gas-u. Wasserfach*, 79, 450-4 (1936)—C.A. 30, 6167.
1449. L. Schwarz and G. Münchmeyer, *Z. f. Hyg. u. Infekt. Krankh.*, 75, 81-100—C.A. 8, 2766.
1450. B. I. Scoggin and G. H. Burruss, *Petroleum Refiner*, 22, 307 (1943); *Oil Gas J.*, 42, No. 24, 61-4, 84, 85 (1943)—C.A. 37, 6859; 38, 4418.
1451. E. M. Scott and W. M. Sandstrom, *Arch. Biochem.*, 1, 103-9 (1942)—C.A. 37, 391.
1452. N. D. Scott to Du Pont Co., U.S. pat. 2,048,169 (1936)—C.A. 30, 6184.

1453. Ruth P. Scott, executrix of the estate of Winfield Scott, deceased, to Wingfoot Corp., U.S. pat. 2,404,103 (1946)—C.A. 40, 6500.
1454. William Seaman to S. O. Dev. Co., (a) U.S. pat. 1,993,287 (1935); (b) 2,035,098 (1936)—C.A. 29, 2547; 30, 3121.
1455. William Seaman and J. R. Huffman to S. O. Dev. Co., U.S. pat. 2,066,189 (1936)—C.A. 31, 1038.
1456. N. F. Sedykh, *Neftyanoe Khoz.*, 18, No. 10, 20-2 (1937); *Chimie & industrie*, 39, 1094—C.A. 32, 7708.
1457. Sigbert Seelig, Ger. pat. 472,070 (1927)—C.A. 23, 2567.
- 1457.5. William Segal and R. L. Starkey, *Anal. Chem.*, 25, 1645-8 (1953)—C.A. 48, 2522.
1458. J. D. Seguy to U. O. Prods. Co., U.S. pat. 1,986,228 (1935)—C.A. 29, 1241.
1459. Leon Selitrenny, *Monatsh.*, 10, 908-17 (1889).
1460. A. Y. Semenova and D. L. Gol'dshtein, *Neftyanoe Khoz.*, 1939, No. 2, 31-5—C.A. 33, 7541.
1461. H. G. Semmes to Standard-I. G. Co., U.S. pat. 1,940,651, 1,940,652, 1,940,653 (1933)—C.A. 28, 1519.
1462. W. B. Shanley and R. E. Sutherland to U. O. Prods. Co., U.S. pat. 2,225,847 (1940)—C.A. 35, 2710.
- 1462.5. Sharples Chemicals Inc., Brit. pat. 555,503 (1943)—C.A. 39, 710.
1463. J. A. Shaw, *Anal. Chem.*, 12, 668-71 (1940)—C.A. 35, 53.
1464. J. J. Shedlock and Optime Motor Spirit Syndicate, Brit. pat. 1,878, of 1914—C.A. 9, 1994.
1465. Shell Development Co., Brit. pat. 597,655 (1948)—C.A. 42, 4338.
1466. Shell Development Co. and E. W. Zublin, Brit. pat. 601,978 (1948)—C.A. 42, 8462.
1467. Shell Oil Co., Fr. pat. 718,305 (1931); Ger. pat. 545,214 (1931)—C.A. 26, 3100, 3101.
1468. M. M. Sherasimov *et al.*, *Neftyanoe Khoz.*, 20, No. 6, 43-5 (1939)—C.A. 34, 3483.
1469. W. H. Shiffler, U.S. pat. 1,865,797 (1932)—C.A. 26, 4464.
1470. W. H. Shiffler and L. P. Elliott to S. O. Co. of Calif., U.S. pat. 2,336,896 (1943)—C.A. 38, 3825.
1471. W. H. Shiffler, M. M. Holm, and M. F. Miller, U.S. pat. 1,869,781 (1932)—C.A. 26, 5413.
1472. Kamenosuke Shinohara, *Am. J. Med. Sci.*, 182, 880-1 (1931); *J. Biol. Chem.*, 96, 285-97 (1932)—C.A. 26, 3171, 4305.

1473. Kamenosuke Shinohara and Martin Kilpatrick, *J. Am. Chem. Soc.*, **56**, 1466-72 (1934)—C.A. **28**, 5319.
1474. A. J. Shmidl and Mehemet Wiggen to S. O. Dev. Co., U.S. pat. 2,356,704 (1944)—C.A. **39**, 181.
1475. G. H. Short to Phillips Petroleum Co., U.S. pat. 2,216,856 (1941)—C.A. **35**, 1624.
1476. D. A. Shtrom and A. V. Fateev, *Zavodskaya Lab.*, **11**, 861 (1945)—C.A. **40**, 7580.
1477. G. Shumovskii, *Groznenskii Neftyanik*, **2**, No. 5-6, 59-61 (1932)—C.A. **26**, 5744.
1478. L. E. Shvartsburd and I. A. Soiferman, *Zavodskaya Lab.*, **15**, 387-94 (1949)—C.A. **43**, 6940.
1479. Silesia, Verein Chem. Fabr., Fr. pat. 786,126 (1935)—C.A. **30**, 1068.
1480. Silesia, Verein Chem. Fabr. (Gerhard Källner), Ger. pat. 613,068 (1935)—C.A. **29**, 5460.
1481. Silica Gel Corp., (a) Fr. pat. 630,081 (1927); (b) 641,695 (1927)—C. **1928**, I, 779; C.A. **23**, 1253.
1482. Daisy G. Simonsen, *J. Biol. Chem.*, **101**, 35-42 (1933)—C.A. **27**, 5088.
1483. James Simpson to S. O. Dev. Co., U.S. pat. 1,718,713 (1929)—C.A. **23**, 4060.
1484. Syndicat d'Études des Matières Organiques, Fr. pat., 642,305 (1927)—C.A. **23**, 1253.
1485. F. S. Sinnatt, *Gas J.*, **208**, 433-8 (1934); *Gas World*, **101**, 556-9—C.A. **29**, 578.
1486. D. W. Sissingh, (a) *Brennstoff-Chem.*, **4**, 112-8 (1923); (b) *ibid.*, **5**, 22-5 (1925); (c) *ibid.*, **234**—C.A. **17**, 2953; **19**, 1491, 167.
1487. Bertil Sjöberg, *Svensk Kem. Tid.*, **50**, 250-4 (1938)—C.A. **33**, 2106.
1488. N. P. Skerrett and H. W. Thompson, *Trans. Faraday Soc.*, **37**, 81-2 (1941)—C.A. **35**, 3175.
1489. K. H. Slagle and E. E. Reid, *Ind. Eng. Chem.*, **24**, 448-51 (1932)—C.A. **26**, 2698.
1490. H. T. Slemmer, U.S. pat. 52,897 (1866).
1491. R. G. Sloane to S. O. Dev. Co., U.S. pat. 1,966,050 (1934)—C.A. **28**, 5653.
1492. W. M. Sloane, U.S. pat. 109,772 (1870).
1493. C. A. Smith, U.S. pat. 558,747 (1896).
1494. C. L. Smith and W. G. Annable to Pure Oil Co., U.S. pat. 2,032,896 (1936)—C.A. **30**, 2744.
1495. H. G. Smith to Gulf Refg. Co., U.S. pat. 1,813,642 (1931)—C.A. **25**, 5280.

1496. H. M. Smith and O. C. Blade, *Oil Gas J.*, 46, No. 30, 73-8 (1947)—C.A. 42, 2745.
1497. L. B. Smith and G. W. Jamison to Atlantic Refg. Co., U.S. pat. 1,676,294 (1928)—C.A. 22, 3289.
1498. Marvin Smith to U. O. Prods. Co., U.S. pat. 1,889,388 (1933)—C.A. 27, 1497.
1499. O. K. Smith and G. T. Williams, *Gas Age*, 84, No. 3, 14-6 (1939)—C.A. 34, 6043.
1500. S. C. Smith, *Oil Gas J.*, 36, No. 47, 44 (1938); *Refiner Natural Gasoline Mfr.*, 17, 138-9 (1938)—C.A. 32, 7708.
1501. Watson Smith, *Brit. pat.* 2025 of 1880.
1502. W. A. Smith, *Ger. pat.* 108,364 (1897)—C. 1900, I, 1007.
1503. W. A. Smith, (a) U.S. pat. 1,938,116 (1933); (b) 1,938,117 (1933); 1,964,087 (1934)—C.A. 28, 1178, 5224.
1504. W. V. Smith, *J. Am. Chem. Soc.*, 68, 2059-64, 2064-9, 2069-71 (1946)—C.A. 41, 1130, 1131.
1505. M. Smolak and F. L. Nelson, *Petroleum Refiner*, 27, No. 8, 405-9 (1948)—C.A. 43, 384.
1506. W. O. Snelling, U.S. pat. 1,215,732 (1917)—C.A. 11, 1296.
1507. R. D. Snow and F. E. Frey, *Ind. Eng. Chem.*, 30, 176-82 (1938)—C.A. 32, 2505.
1508. H. R. Snyder and G. W. Cannon, *J. Am. Chem. Soc.*, 66, 155-6 (1944)—C.A. 38, 954.
1509. H. R. Snyder and E. L. Eliel, *J. Am. Chem. Soc.*, 70, 2825-6 (1948)—C.A. 42, 8159.
1510. H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, 69, 2672-4 (1947)—C.A. 42, 1881.
1511. L. J. Snyder, U.S. pat. 1,985,955 (1935)—C.A. 29, 1240.
1512. Soc. Anon. St. Denis, *Ger. pat.* 79,505 (1894)—C. 1895, I, 943.
1513. Societa italiana per le industrie minerale e chimiche, *Brit. pat.* 315,459 (1928)—C.A. 24, 1735.
1514. Soc. Nouvelle des Mines de St. Champs, *Fr. pat.* 707,705 (1930)—C.A. 26, 838.
1515. Soc. des usines chim. Rhône-Poulenc, *Fr. pat.* 753,401 (1933)—C.A. 28, 1140.
1516. A. Sommer, U.S. pat. 523,716, 525,969 (1894).
1517. Denise Sontag, *Ann. chim.*, [11] 1, 359-438 (1934)—C.A. 28, 4716-8.
- 1517.5. Q. F. Soper, W. E. Buting, J. E. Cochran, Jr., and Albert Pohland, *J. Am. Chem. Soc.*, 76, 4109-12 (1954)—C.A. 49, 5287.
1518. Mott Souders, Jr., and G. G. Brown, *Ind. Eng. Chem.*, 24, 519-22 (1932)—C.A. 26, 3416.

1519. W. J. Sparks to Du Pont Co., U.S. pat. 2,042,557 (1936)—C.A. 30, 5023.
1520. C. C. Sperling to Petroleum Conversion Corp., U.S. pat. 2,319,354 (1943)—C.A. 37, 6875.
1521. Spettmann, *Technische Blätter*, 5, 131 (1915); *Chem. Ztg.*, 40, Rep. 231 (1916).
1522. E. R. Speyer, Expt. & Res. Station, Chestnut, Herts, 8th Ann. Rept., 45–57 (1922).
1523. Otto Sprenger, Brit. pat. 3,074 of 1909—C. A. 4, 2569.
1524. C. Staemmler, *Brennstoff-Chem.*, 12, 43–5 (1931)—C.A. 25, 1659.
1525. B. A. Stagner, *Ind. Eng. Chem.*, 27, 275–7 (1935); *Oil Gas J.*, 33, No. 50, 62–4 (1935)—C.A. 29, 2716, 6411.
1526. B. A. Stagner, U.S. pat. 1,970,583 (1934)—C.A. 28, 6295.
1527. I. J. Staid and J. E. Murphy to S. O. Dev. Co., U.S. pat. 2,370,819 (1945)—C.A. 39, 4469.
1528. F. R. Staley, *Natl. Petroleum News*, 19, No. 49, 88, 90 (1927)—C.A. 22, 681.
1529. Standard Oil Co. of Ohio, Fr. pat. 796,424 (1936)—C.A. 30, 6145.
1530. Standard Oil Development Co., (a) Brit. pat. 550,715 (1943); (b) 553,100 (1943); (c) 560,839 (1944); (d) Ger. pat. 607,986 (1932)—C.A. 38, 1873, 5393; 40, 3890; C. 1935, I, 2256.
1531. Standard Oil Development Co., (a) Fr. pat. 658,889 (1929); (b) 701,366 (1930); (c) 712,580 (1931); (d) 832,721 (1938); Brit. pat. 497,255 (1938)—C. 1930, I, 780; C.A. 25, 4115; 26, 2047; 33, 2694, 4011.
1532. E. A. Starke, U.S. pat. 597,920 (1898).
1533. H. W. Starkweather and A. M. Collins to Du Pont Co., U.S. pat. 2,234,203 (1941)—C.A. 35, 3742.
1534. Norbert Steiger to Hoffmann-La Roche Inc., U.S. pat. 2,490,717 (1949)—C.A. 44, 3527.
1535. A. Steigmann, *J. Soc. Chem. Ind.*, 61, 18–9 (1942)—C.A. 36, 3454.
1536. M. J. Sterba, *Ind. Eng. Chem.*, 41, 2680–7 (1949)—C.A. 44, 2213.
1537. D. R. Stevens and W. A. Gruse to Gulf Refg. Co., U.S. pat. 1,999,345, 2,001,634 (1935)—C.A. 29, 4165, 4568.
1538. L. Stevens, U.S. pat. 414,601 (1889).
1539. Alexander Stewart to Natl. Lead Co., U.S. pat. 2,110,745 (1938)—C.A. 32, 3602.
1540. L. C. Stewart and Lee DePree to Dow Chem. Co., U.S. pat. 1,917,073 (1933)—C.A. 27, 4539.

- 1540.5. W. T. Stewart and J. O. Clayton to Calif. Research Corp., U.S. pat. 2,543,734, 2,543,735 (1951)—C.A. 45, 4033.
1541. J. S. Stewart-Wallace, Belg. pat. 152,278 (1900).
1542. J. S. Stewart-Wallace and W. B. Cowell, Brit. pat. 9,796 of 1900.
1543. F. W. Stone and J. N. Garrison, U.S. pat. 2,022,550 (1935)—C.A. 30, 850.
1544. H. Strache and P. Porges, U.S. pat. 1,205,578 (1916)—C.A. 11, 207.
1545. N. Strafford, F. R. Cropper, and A. Hamer, Analyst, 75, 55-6 (1950)—C.A. 44, 3409.
1546. L. C. Strang and Jack Owen to Anglo-Iranian Oil Co. Ltd., Brit. pat. 588,765 (1947)—C.A. 41, 6706.
1547. Siegmund Stransky and F. Hansing, Brit. pat. 267,959 (1926)—C.A. 22, 1232.
1548. C. W. Stratford to S. O. of Calif., U.S. pat. 2,308,755 (1943)—C.A. 37, 4240.
1549. C. W. Stratford, F. G. Graves, and E. S. Brown, Refiner, 17, No. 3, 109-14, 120 (1938)—C.A. 32, 4320.
1550. C. W. Stratford and D. B. Nutt, II Congr. mondial pétrole, 2, Sect. 2, Phys., chim., raffinage, 407-11 (1937)—C.A. 33, 354.
1551. R. K. Stratford to Imperial Oil Ltd., Can. pat. 278,179 (1928)—C.A. 22, 2835.
1552. R. K. Stratford to S. O. Dev. Co., (a) Can. pat. 308,405 (1931); U.S. pat. 1,860,823 (1932); (b) Brit. pat. 369,737 (1930); (c) U.S. pat. 2,336,651 (1943)—C.A. 25, 1376; 26, 3915; 27, 2294; 38, 3813.
1553. R. K. Stratford and W. P. Doohan to S. O. Dev. Co., (a) Can. pat. 312,866 (1931); (b) 334,378 (1933); (c) U.S. pat. 1,904,173 (1933)—C.A. 25, 4396; 27, 5529, 3325.
1554. W. M. Stratford to The Texas Co., U.S. pat. 2,078,468 (1937)—C.A. 31, 4491.
1555. B. R. Strickland to S. O. Dev. Co., U.S. pat. 2,339,889 (1944)—C.A. 38, 4421.
- 1555.5. Walter Stricks and I. M. Kolthoff, J. Am. Chem. Soc., 75, 5673-81 (1953)—C.A. 48, 10588.
1556. D. A. Strom and N. M. Shestokova, Neftyanoe Khoz., 24, No. 3-4, 68-70 (1946)—C.A. 41, 589.
1557. Murray Stuart and L. M. Stuart, Brit. pat. 367,848 (1930)—C.A. 27, 2293.
1558. Studien-u. Verwertungs-G.m.b.H. (Otto Roelen and Walter Feisst), Ger. pat. 651,462 (1937)—C.A. 32, 1434.

1559. Philip Subkow to Union Oil Co. of Calif., U.S. pat. 2,081,310 (1937)—C.A. 31, 5156.
1560. J. J. Suckert, U.S. pat. 534,295 (1895).
1561. K. Suesselbeck vested in the Alien Property Custodian, U.S. pat. 2,308,249 (1943)—C.A. 37, 3924.
1562. F. W. Sullivan, Jr., to S. O. Co. of Ind., U.S. pat. 2,034,495 (1936)—C.A. 30, 3222.
1563. F. W. Sullivan, Jr., and A. B. Brown to S. O. Co. of Ind., U.S. pat. 1,938,670, 1,938,671 (1933)—C.A. 28, 1520.
1564. M. C. Sumpter to U. O. Prods. Co., (a) U.S. pat. 1,912,603 (1933); (b) 1,971,167 (1934)—C.A. 27, 4386; 28, 6295.
1565. E. D. Sutton to Pure Oil Co., U.S. pat. 2,157,223 (1939)—C.A. 33, 6581.
1566. L. E. Sutton, *J. Am. Med. Assoc.*, 104, 2168-71 (1935)—C.A. 29, 6650.
1567. L. E. Sutton to Chemical Foundation, U.S. pat. 1,926,797 (1933)—C.A. 27, 5895.
1568. L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, 52, 651-60 (1930)—C.A. 24, 1340.
1569. D. Symonds, (a) U.S. pat. 65,136 (1867); (b) 65,137 (1867).
1570. Antoni Szayna to A. C. Travis, (a) U.S. pat. 2,273,297 (1942); (b) 2,273,298, 2,273,299 (1942); (c) 2,337,358 (1943)—C.A. 36, 4327, 4326; 38, 3813.
1571. L. von Szeszich and R. Hupe, *Brennstoff-Chem.*, 14, 221-5 (1933)—C.A. 27, 4901.
- 1571.5. Seishi Takagi, Hisashi Tanaka, and Hiroaki Tsukatani, *Bull. Inst. Chem. Research, Kyoto Univ.*, 27, 72 (1951)—C.A. 47, 111.
1572. M. W. Tamele and L. B. Ryland, *Anal. Chem.*, 8, 16-9 (1936)—C.A. 30, 1329.
1573. M. W. Tamele, L. B. Ryland, and V. C. Irvine, *Anal. Chem.*, 13, 618-22 (1941)—C.A. 35, 6899.
1574. D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, 49, 1-90 (1951).
1575. H. S. Tasker and H. O. Jones, *J. Chem. Soc.*, 95, 1904-9 (1909)—C.A. 4, 1023.
1576. J. A. Tatro, U.S. pat. 106,233 (1870).
1577. J. Tausz, *Z. angew. Chem.*, 41, 628 (1928).
1578. H. A. Taylor and E. T. Layng, *J. Chem. Phys.*, 1, 798-808 (1933)—C.A. 28, 702.

1579. H. K. Taylor and D. M. Graham, U.S. pat. 54,978 (1866).
1580. H. S. Taylor, (a) Refiner Natural Gasoline Mfr., 9, No. 12, 83 (1930); (b) Can. Chem. Processes Ind., 26, 339-40 (1942)—C.A. 25, 1370; 36, 5339.
1581. J. F. H. Taylor and H. I. Lounsbury to Shell Dev. Co., U.S. pat. 2,025,255 (1935)—C.A. 30, 1223.
1582. M. C. Taylor, U.S. pat. 1,908,273 (1933)—C.A. 27, 3810.
1583. C. F. Teichmann, U.S. pat. 2,011,954 (1935)—C.A. 29, 6751.
1584. A. J. Tempere, U.S. pat. 557,291 (1896).
1585. Irmgard Teutsch, Petroleum Z., 30, No. 20, 1-6 (1934)—C.A. 28, 4872.
1586. Texaco Dev. Corp., (a) Fr. pat. 761,270 (1934); (b) 765,218 (1934)—C.A. 28, 4218, 6995.
1586.3. C. M. Thacker and R. T. Bell to Pure Oil Co., U.S. pat. 2,409,080 (1946)—C.A. 41, 1242.
1586.5. C. M. Thacker and R. C. Swann to Pure Oil Co., U.S. pat. 2,423,530 (1947)—C.A. 42, 3777.
1587. R. B. Thacker, Jr., to Sinclair Refg. Co., (a) U.S. pat. 1,994,969 (1935); (b) 2,340,157 (1944)—C.A. 29, 3149; 38, 4429.
1588. F. C. Thiele, U.S. pat. 683,354 (1901).
1589. F. C. Thiele, I. M. Parker, and J. T. Finke, Ger. pat. 133,426 (1901)—C. 1902, II. 555.
1590. E. H. Thierry, J. Chem. Soc., 127, 2756-9 (1925)—C.A. 20, 984.
1591. F. B. Thole, S. F. Birch, and W. S. G. P. Norris, Brit. pat. 288,931 (1926)—C.A. 23, 695.
1592. F. B. Thole and S. T. Card to Anglo-Iranian Oil Co., Brit. pat. 231,944 (1924); U.S. pat. 1,776,340 (1930)—C.A. 19, 3586; 24, 5476.
1593. C. A. Thomas and Wilhelm Schmidt-Nickels to Sharples Solvents Corp., U.S. pat. 2,068,614 (1937)—C.A. 31, 1917.
1594. D. L. Thomas, U.S. pat. 1,781,826, 1,781,963 (1930)—C.A. 25, 409.
1594.5. C. J. Thompson, R. A. Meyer, and J. S. Ball, J. Am. Chem. Soc., 74, 3284-7, 3287-9 (1952)—C.A. 47, 5876.
1594.7. R. B. Thompson to U. O. Prods. Co., U.S. pat. 2,553,797 (1951)—C.A. 46, 7579.
1595. Sijbren Tijmstra, Brit. pat. 318,706 (1928)—C.A. 24, 2284.

1596. Sijbren Tijmstra to Roxana Petroleum Co., U.S. pat. 1,684,159 (1928)—C.A. 22, 4242.
1597. Sijbren Tijmstra to Simplex Refg. Co., Can. pat. 283,795 (1928)—C.A. 22, 4788.
1598. I. N. Tits-Skvortsova, A. I. Leoniva, and S. Y. Levina, *Doklady Akad. Nauk SSSR*, 80, 377–80 (1951); *ibid.*, 84, 741–3 (1952); *ibid.*, 88, 1007–10 (1953)—C.A. 46, 5009; 47, 3247; 48, 8752.
- 1598.5. I. N. Tits-Skvortsova, A. I. Leonova, S. Y. Levina, and E. A. Karaseva, *Zhur. Obshehei Khim.*, 23, 303–10 (1953)—C.A. 48, 2637.
1599. I. N. Tits-Skvortsova, S. Y. Levina, A. I. Leonova, and E. A. Karaseva, *Zhur. Obshehei Khim.*, 21, 242–50 (1951)—C.A. 45, 7514.
- 1599.5. Suzanne Tocaven, *Compt. rend.*, 234, 1581–3 (1952)—C.A. 47, 6593.
1600. James Toman, *Growth*, 3, 419–25 (1940)—C.A. 34, 4469.
1601. K. Tomekichi, *J. Soc. Chem. Ind. (Japan)*, 30, 129–35 (1927).
1602. J. A. Tones, *Gas J.*, 245, 185–6 (1945)—C.A. 39, 1747.
1603. A. Travers and P. Marecaux, 14me. Congr. chim. ind., Paris, Oct., 1934, 6 p.—C.A. 29, 6747.
1604. N. R. Trenner and H. A. Taylor, *J. Chem. Phys.*, 1, 77–88, 286 (1933)—C.A. 27, 1809, 3133.
1605. M. J. Trumble, U.S. pat. 1,725,320 (1929)—C.A. 23, 4815.
1606. A. W. Trusty, (a) *Refiner Natural Gasoline Mfr.*, 19, No. 4, 93–6 (1940); (b) *Petroleum Engr.*, 13, No. 4, 58, 60, 62 (1942); (c) *ibid.*, No. 8, 72–4, 76–7 (1942)—C.A. 34, 4550; 36, 1763, 4699.
1607. Eduard Tschunkur and Hugo Köhler to I. G. Farben., U.S. pat. 2,064,395 (1936)—C.A. 31, 709.
1608. I. I. Tsyganok and L. A. Vanyukov, *Neft*, 1940, No. 9, 36–8; *Petroleum Engr.*, 14, No. 11, 75–6 (1943)—C.A. 37, 6868; 38, 4416.
1609. Ernest Turk and E. E. Reid, *Anal. Chem.*, 17, 713–4 (1945)—C.A. 40, 534.
1610. H. G. Turley and Wallace Windus, *Stiasny Festschr.*, 1937, 396–406—C.A. 32, 8183.
1611. H. G. Turley and Wallace Windus to Röhm and Haas, U.S. pat. 1,973,130 (1934)—C.A. 28, 7068.
1612. L. B. Turner to S. O. Dev. Co., U.S. pat. 2,028,303 (1936)—C.A. 30, 1393.

1613. Yosio Tutiya, J. Agr. Chem. Soc. Japan, 17, 465-75; Bull. Agr. Chem. Soc. Japan, 17, 48-9 (1941) (English)—C.A. 36, 3752.
1614. R. B. Tuttle, (a) Oil Gas J., 43, No. 45, 85-6 (1945); (b) *ibid.*, 46, No. 19, 84-5, 108-9 (1947)—C.A. 39, 2194; 41, 7714.
1615. A. N. Tyler, U.S. pat. 38,015 (1863).
1616. Hans Ufer to I. G. Farben., Ger. pat. 528,915 (1926)—C.A. 26, 1045.
1617. Henry Ulrich, U.S. pat. 1,810,803 (1931)—C.A. 25, 4697.
1618. A. J. V. Underwood, Ind. Chemist, 10, 128-30 (1934)—C.A. 28, 3809.
1619. Universal Oil Products Co., Fr. pat. 736,834 (1932)—C.A. 27, 1499.
1620. Wilhelm Urban to Hydrierwerk Scholven A.-G., Ger. pat. 722,594 (1942)—C.A. 37, 5223.
1621. K. S. Valentine and G. MacLean, Refiner Natural Gasoline Mfr., 14, No. 10, 475-8 (1935)—C.A. 29, 8303.
1622. C. H. Van Hartesveldt and H. W. Field, Refiner Natural Gasoline Mfr., 19, No. 6, 93-8 (1940).
1623. Lee VanHorn and L. J. Kelly to The M. W. Kellogg Co., U.S. pat. 2,357,365 (1944)—C.A. 39, 408.
1624. L. Vanino and F. Mussnug, Ber., 50, 21-4 (1917)—C.A. 11, 2784.
1625. H. S. VanTine, U.S. pat. 60,290 (1866).
1626. M. G. Van Voorhis, (a) Natl. Petroleum News, 32, No. 2, R3-6 (1940); (b) *ibid.*, 32, R122, R129 (1940)—C.A. 34, 4552.
1627. Jozsef Varga, (a) Brennstoff-Chem., 9, 277-92 (1928); Kem., Folyóirat, 34, 65-76 (1928); (b) Math. naturw. Anz. ungar. Akad. Wiss., 48, 809-15 (1931); 50, 386-406 (1933)—C.A. 22, 4767; 23, 4796; 27, 1736; 28, 3218.
1628. Jozsef Varga, (a) Fr. pat. 676,464 (1929); (b) 683,069 (1930)—C.A. 24, 3103, 4519.
1629. Jozsef Varga to Deutsche Gold-u. Silber-Scheideanstalt vorm. Roessler, U.S. pat. 1,852,988 (1932); 1,894,924, 1,894,925, 1,894,926 (1933)—C.A. 26, 3091; 27, 2460, 2560.
1630. Jozsef Varga and I. Makray, Brennstoff-Chem., 12, 389-90 (1931)—C.A. 26, 1096.
1631. J. J. Verbanc to Du Pont Co., U.S. pat. 2,413,531 (1946)—C.A. 41, 1704.

1632. V. Vesselovsky and V. A. Kalichevsky, *Ind. Eng. Chem.*, **23**, 181-4 (1931)—C.A. **25**, 1370.
- 1632.4. P. S. Viles to S. O. Dev. Co., U.S. pat. 2,557,018 (1951)—C.A. **45**, 7779.
- 1632.6. P. S. Viles and Elza Q. Camp to S. O. Dev. Co., U.S. pat. 2,474,603 (1949)—C.A. **43**, 7221.
1633. J. R. Vincent to Du Pont Co., U.S. pat. 2,394,952 (1946)—C.A. **40**, 2683.
1634. R. W. Virtue and H. B. Lewis, *J. Biol. Chem.*, **104**, 415-21 (1934)—C.A. **28**, 3096.
1635. N. E. Vishnevskii and R. D. Obolentsev, *J. Applied Chem. (USSR)*, **19**, 881-9 (1946)—C.A. **41**, 4638.
1636. Albert Vita, *Ger. pat.* 384,846 (1923)—C. **1924**, I, 717.
1637. H. Vittenet, *Fr. pat.* 329,076 (1903).
1638. D. L. Vivian and Fred Acree, Jr., U.S. Dept. Agr., Bur. Entomol. Plant Quarantine, *E-539*, 48 p. (1941)—C.A. **35**, 4149.
1639. D. L. Vivian and E. E. Reid, *J. Am. Chem. Soc.*, **57**, 2559-60 (1935)—C.A. **30**, 1741.
1640. V. L. Oil Processes, Ltd., *Fr. pat.* 575,600 (1924)—C. **1925**, I, 1037.
1641. V. L. Oil Processes, Ltd. and O. D. Lucas, *Fr. pat.* 575,598 (1923); *Brit. pat.* 211,664 (1923)—C.A. **18**, 1903.
1642. A. C. Vobach to Sinclair Refg. Co., U.S. pat. 1,736,234 (1929)—C.A. **24**, 718.
1643. Carl Vogt, *Ann.*, **119**, 142-53 (1861).
1644. W. H. Volck to Calif. Spray Chemical Corp., U.S. pat. 2,047,755 (1936)—C.A. **30**, 6181.
1645. G. H. Von Fuchs and L. E. Border to Shell Dev. Co., U.S. pat. 2,080,365 (1937); 2,149,035, 2,174,810 (1939)—C.A. **31**, 5145; **33**, 4415; **34**, 880.
1646. G. H. Von Fuchs and H. H. Zuidema to Shell Dev. Co., *Can. pat.* 403,830; U.S. pat. 2,276,526 (1942)—C.A. **36**, 3957, 5007.
1647. G. H. Von Fuchs and H. H. Zuidema to N. V. Bataafsche, *Ger. pat.* 735,328 (1943)—C.A. **38**, 3828.
1648. Vanderveer Voorhees and E. J. Schaeffer to S. O. Co. of Ind., U.S. pat. 1,810,632 (1931)—C.A. **25**, 4697.
1649. Alexis Voorhies, Jr., and W. M. Smith, *Ind. Eng. Chem.*, **41**, 2708-10 (1949)—C.A. **44**, 2213.
1650. R. S. Vose to Du Pont Co., U.S. pat. 1,952,616, 1,962,698 (1934)—C.A. **28**, 3578, 4897.
- 1650.5. Harman de Vries and T. A. Zuidhof, *Rec. trav. chim.*, **70**, 696 (1951)—C.A. **46**, 8625.

1651. J. M. Wadsworth, U.S. pat. 1,960,561 (1934)—C.A. 28, 4587.
1652. C. R. Wagner, *Oil Gas J.*, 31, No. 45, 58 (1933)—C.A. 27, 3594.
1653. J. F. Wait, (a) U.S. pat. 2,034,068, 2,050,772, 2,059,542, 2,063,860 (1936); 2,075,151 (1937); (b) 2,058,534 (1936)—C.A. 30, 3215, 6936; 31, 532, 853, 3685, 248.
1654. W. R. Waldron and E. E. Reid, *J. Am. Chem. Soc.*, 45, 2399-417 (1923)—C.A. 17, 3863.
- 1654.5. Emmanuel Waletzky to Am. Cyanamid Co., U.S. pat. 2,531,754 (1950)—C.A. 45, 3132.
1655. H. H. Walker to The Texas Co., U.S. pat. 2,328,760 (1943)—C.A. 38, 1352.
1656. H. H. Walker and J. P. Mostyn to The Texas Co., U.S. pat. 2,366,580 (1945)—C.A. 39, 2399.
1657. H. V. Walker to Maas and Waldstein Co., U.S. pat. 955,372 (1910)—C.A. 4, 1669.
1658. H. W. Walker to Du Pont Co., U.S. pat. 2,259,122 (1941)—C.A. 36, 929.
1659. W. R. Walkey and A. F. Bargate, *Brit. pat.* 186,738 (1921)—C.A. 17, 1136.
1660. C. A. Walter and F. B. Muhlenberg, U.S. pat. 1,669,181 (1928)—C.A. 22, 2268.
1661. J. A. Wanklyn and E. Erlenmeyer, *J. Chem. Soc.*, 17, 190-3 (1864).
1662. P. F. Warner and J. A. McBride to Phillips Petroleum Co., U.S. pat. 2,503,644 (1950)—C.A. 44, 5896.
1663. J. W. Warren, (a) U.S. pat. 666,446 (1901); (b) 705,168 (1902).
1664. J. I. Wasson to S. O. Dev. Co., U.S. pat. 2,522,476 (1950)—C.A. 44, 11130.
1665. H. I. Waterman, *J. Inst. Petroleum Tech.*, 11, 576-82 (1925)—C.A. 20, 1711.
1666. H. I. Waterman and J. H. Heimel, *Chem. Weekblad*, 21, 374-5 (1924); *J. Inst. Petroleum Tech.*, 10, 812-5 (1924)—C.A. 18, 3710; 19, 889.
1667. H. I. Waterman and J. N. J. Perquin, (a) *Brennstoff-Chem.*, 6, 255-7 (1925); (b) *Chem. Weekblad*, 22, 389-93 (1923); (c) *J. Inst. Petroleum Tech.*, 11, 560-70 (1925)—C.A. 19, 3371; 20, 1712.
1668. H. I. Waterman, J. N. J. Perquin, W. J. M. Bogaers, and J. R. H. Goris, *Chem. Weekblad*, 22, 378-80 (1925)—C.A. 19, 3158.

1669. H. I. Waterman and D. W. Sissingh, *Chem. Weekblad*, **19**, 489-92 (1922); *Brennstoff-Chem.*, **4**, 30 (1923)—C.A. **17**, 1133.
1670. H. I. Waterman and M. J. van Tussenbroek, (a) *Brennstoff-Chem.*, **8**, 20-1 (1927); **9**, 397-8 (1928); (b) *ibid.*, **9**, 37-9 (1928); (c) *Erdöl u. Teer*, **3**, 743-4 (1927)—C.A. **21**, 1540; **23**, 2816; **22**, 2528, 572.
1671. C. E. Waters, (a) U.S. Bur. Standards, *Tech. Paper*, **177** (1920); *Ind. Eng. Chem.*, **12**, 482-5, 612 (1920); (b) *ibid.*, **14**, 725-7 (1922)—C.A. **15**, 594; **16**, 3752.
1672. C. B. Watson, U.S. pat. 1,474,395 (1924)—C.A. **18**, 584.
1673. C. B. Watson to Pure Oil Co., U.S. pat. 2,064,999 (1936)—C.A. **31**, 843.
1674. K. M. Watson to U. O. Prods. Co., U.S. pat. 2,315,144 (1943)—C.A. **37**, 5856.
1675. F. W. Weber, U.S. pat. 1,636,946 (1927)—C.A. **21**, 3126.
1676. C. Wegner, Can. pat. 273,682 (1927)—C.A. **21**, 4060.
1677. Bengt Wejbull, *Arkiv Kemi, Mineral Geol.*, **23A**, No. 18, 25 p. (1946)—C.A. **44**, 1427.
1678. E. Weingaertner and Herbert Kunze to Braunkohle-Benzin A.-G., Ger. pat. 724,911 (1942)—C.A. **37**, 5850.
1679. J. W. Weir, U.S. pat. 1,564,501 (1925); 1,581,369, 1,603,174 (1926)—C.A. **20**, 502, 1903, 3805.
1680. Joseph Weiss and Harry Fishgold, *Nature*, **137**, 71-2 (1936)—C.A. **30**, 2494.
1681. J. M. Weiss to Barrett Co., U.S. pat. 1,206,962 (1916)—*J. Soc. Chem. Ind.*, **36**, 129 (1917).
1682. Ulrich Weiss to Endo Products, Inc., U.S. pat. 2,520,293 (1950)—C.A. **46**, 134.
1683. Rudolf Weissgerber, Otto Kruber, and Wilhelm Thies to G. für Teerverwertung, Ger. pat. 483,759 (1929)—C.A. **24**, 626.
1684. A. F. Wells, *Z. Kryst.*, **96**, 435-50 (1937)—C.A. **31**, 8303.
1685. W. C. Wells and F. E. Wells, U.S. pat. 1,296,244 (1919)—C.A. **13**, 1528.
1686. G. L. Wendt, *Petroleum Age*, **15**, No. 1, 16-7 (1925)—C.A. **19**, 1343.
1687. G. L. Wendt, (a) U.S. pat. 1,594,083 (1926); (b) 1,658,505 (1938); (c) 1,668,225 (1928)—C.A. **20**, 3235; **22**, 1233, 2267.
1688. G. L. Wendt to S. O. Co. of Ind., U.S. pat. 1,791,179 (1931)—C.A. **25**, 1667.
1689. G. L. Wendt and S. H. Diggs, *Ind. Eng. Chem.*, **16**, 1113-5 (1924)—C.A. **19**, 395.

1690. H. H. Wenzke and F. C. Moriarty, *Oil Gas J.*, 32, No. 23, 43-7, 73-5 (1943)—C.A. 39, 3655.
1691. A. E. A. Werner, *Sci. Proc. Roy. Dublin Soc.*, 22, 387-92 (1941)—C.A. 35, 5415.
1692. Heinrich Werner, *Swiss pat.* 154,183 (1932)—C. 1932, II, 3183.
1693. J. H. Werntz to Du Pont Co., *U.S. pat.* 2,142,162, 2,187,-338, 2,187,339 (1940)—C.A. 33, 3031; 34, 3404.
1694. E. Wertheim, *J. Am. Chem. Soc.*, 51, 3661-4 (1929)—C.A. 24, 336.
- 1694.5. H. L. Wheeler and T. B. Johnson, *Am. Chem. J.*, 26, 185-206 (1901).
1695. R. C. Wheeler and P. W. Prutzman, *U.S. pat.* 1,728,156 (1929)—C.A. 23, 5312.
1696. Harry Whitaker to Petroleum Processes Corp., *U.S. pat.* 1,952,482 (1934)—C.A. 28, 3574.
1697. J. R. Whiting and W. A. Lawrence, *U.S. pat.* 583,779 (1897).
1698. J. C. Whitman, *U.S. pat.* 1,312,375 (1919)—C.A. 13, 2594.
1699. Gustav Wietzel, Josef Jannek, and Fritz Fried to I. G. Farben., *U.S. pat.* 1,782,590 (1930)—C.A. 25, 400.
1700. P. J. Wiezevich, L. B. Turner, and P. K. Frolich, *Ind. Eng. Chem.*, 25, 295-6 (1933)—C.A. 27, 2021.
1701. P. F. Wiley, *J. Org. Chem.*, 16, 810-4 (1951)—C.A. 46, 1481.
1702. R. M. Wilhelm, *Tag Manual for Inspectors of Petroleum*, 23rd. Ed., C. J. Tagliabue Mfg. Co., Brooklyn, N. Y.
1703. F. E. Wilkinson, *U.S. pat.* 2,303,970 (1942)—C.A. 37, 3262.
- 1703.5. C. Willgerodt, *Ber.*, 18, 331-3 (1885).
1704. C. G. Williams, *J. Inst. Automobile Engrs. (London)*, 1, No. 8, 73-92 (1933); 2, No. 10, 19-34 (1934)—C.A. 28, 6989.
1705. E. C. Williams and H. P. A. Groll to Shell Dev. Co., *U.S. pat.* 1,939,839 (1933)—C.A. 28, 1522.
1706. F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, 53, 352-6 (1931)—C.A. 25, 911.
1707. Keith Williams, *Australian pat.* 123,246 (1947); *Brit. pat.* 598,557 (1948)—C.A. 42, 1731, 5656.
1708. A. L. Wilson and H. R. Fife to Carbide and Chemicals Corp., *U.S. pat.* 2,238,201 (1941)—C.A. 35, 5301.
1709. H. H. Wilson, *Can. pat.* 278,381 (1928)—C.A. 22, 2835.

1710. H. H. Wilson to S. O. Dev. Co., U.S. pat. 1,805,444 (1931)—C.A. 25, 3822.
1711. J. G. Wilson to Shell Dev. Co., U.S. pat. 2,351,467 (1944)—C.A. 38, 6087.
1712. Louise P. Wilson, *Growth*, 3, 409–17 (1940)—C.A. 34, 4469.
1713. P. J. Wilson, Jr., J. H. Wells and Pauline M. Sommerfeld to Carnegie-Illinois Steel Corp., U.S. pat. 2,427,988 (1947)—C.A. 42, 347.
1714. R. E. Wilson and W. H. Bahlke, *Ind. Eng. Chem.*, 17, 355–8 (1925)—C.A. 19, 1398.
1715. V. W. Wilson, *Refiner Natural Gasoline Mfr.*, 18, No. 3, 96–100 (1940).
1716. V. W. Wilson to Buffalo Electro-Chemical Co., (a) U.S. pat. 2,181,036, 2,181,037 (1939); (b) 2,233,802 (1941)—C.A. 34, 1842; 35, 4192.
1717. G. S. Windle, *Petroleum Refiner*, 23, 41–5 (1944)—C.A. 38, 1867.
1718. G. S. Windle to S. O. Co. of Calif., U.S. pat. 2,344,910 (1944)—C.A. 38, 4429.
1719. Wallace Windus and H. G. Turley, *J. Am. Leather Chem. Assoc.*, 33, 246–53 (1938)—C.A. 32, 8821–2.
1720. J. N. Wingett, U.S. pat. 1,185,747 (1916).
1721. C. Winssinger, *Bull. Belg.*, (3) 4, No. 8 (1882); *Bull. Belg. Acad.* (3) 14, 760 (1887)—*Bull. soc. chim.*, [2] 48, 109–11 (1887); *J.*, 1887, 1280.
1722. Charles Wirth, III, and W. B. Shanley to U. O. Prods. Co., U.S. pat. 2,236,080 (1941)—C.A. 35, 4587.
1723. Charles Wirth, III, and J. R. Strong, *Anal. Chem.*, 8, 344 (1936)—C.A. 30, 7828.
1724. H. Wohl, *Dingler's Polytech. J.*, 216, 47–51 (1875).
1725. A. E. Wood, (a) *J. Am. Chem. Soc.*, 47, 2062 (1925); (b) *Oil Gas J.*, 25, No. 40, 147, 158 (1927)—C.A. 19, 2473; 21, 1541.
1726. A. E. Wood, A. R. Greene, and R. W. Provine, *Ind. Eng. Chem.*, 18, 823–6 (1926)—C.A. 21, 1004.
1727. A. E. Wood, A. Lowy, and W. F. Faragher, *Ind. Eng. Chem.*, 16, 1116–20 (1924)—C.A. 19, 395.
1728. A. E. Wood, Clyde Sheely, and A. W. Trusty, *Ind. Eng. Chem.*, 17, 798–802 (1925)—C.A. 19, 3471.
1729. W. R. Wood to Girdler Corp., U.S. pat. 2,220,138 (1940)—C.A. 35, 1982.
1730. G. M. Woods, *Refiner Natural Gasoline Mfr.*, 14, No. 10, 479 (1935)—C.A. 29, 8306.

1731. Gladys E. Woodward, (a) *Ind. Eng. Chem.*, **21**, 693-5 (1929); (b) *ibid.*, 1233-5; (c) *Anal. Chem.*, **1**, 117-8 (1929)—C.A. **23**, 4051; **24**, 1206; **23**, 4332.
1732. Paul Woog vested in Alien Property Custodian, U.S. pat. 2,352,059 (1944)—C.A. **38**, 6087.
1733. A. R. Workman to Cities Service Oil Co., U.S. pat. 2,338,371 (1944)—C.A. **38**, 4429.
1734. C. J. Wright, *J. Inst. Petroleum Tech.*, **15**, 214-44 (1929)—C.A. **23**, 4054.
1735. Rudolf von Wülfig and Ernst Rosskoth (trading as J. A. Wülfig), Ernst Sturm, and Richard Fleischmann, *Brit. pat.* 473,240 (1937)—C.A. **32**, 1716.
1736. Henri Wuyts, *Ber.*, **36**, 863-70 (1903).
1737. E. W. Wynne, U.S. pat. 901,411 (1908)—C.A. **3**, 591.
1738. John Xan, E. A. Wilson, L. D. Roberts, and N. H. Horton, *J. Am. Chem. Soc.*, **63**, 1139-41 (1941)—C.A. **35**, 3594.
1739. D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257-62 (1940)—C.A. **34**, 3066.
1740. D. L. Yabroff to N. V. Bataafsche, (a) *Brit. pat.* 494,451 (1938); (b) 502,448 (1939); (c) 499,678, 506,574 (1939); *Ger. pat.* 724,397 (1942)—C.A. **33**, 3133, 7091, 5173; **34**, 114.
1741. D. L. Yabroff to Shell Dev. Co., (a) U.S. pat. 2,152,166 (1939); (b) 2,152,720, 2,152,723, 2,168,078 (1939); *Can. pat.* 380,235 (1939)—C.A. **33**, 5001, 5173, 5174, 9621, 4011.
1742. D. L. Yabroff to Shell Dev. Co., (a) U.S. pat. 2,152,721 (1939); (b) 2,183,801 (1939); (c) 2,186,398 (1939); (d) 2,212,105 (1940); (e) 2,212,106, 2,212,107 (1940); (f) 2,228,295 (1941)—C.A. **33**, 5173; **34**, 2584, 3487; **35**, 612, 3075.
1743. D. L. Yabroff and L. E. Border, *Refiner Natural Gasoline Mfr.*, **18**, 171-6, 203 (1939)—C.A. **33**, 7540.
1744. D. L. Yabroff and J. W. Givens to N. V. Bataafsche, *Brit. pat.* 469,573 (1937)—C.A. **32**, 761.
1745. D. L. Yabroff and J. W. Givens to Shell Dev. Co., (a) U.S. pat. 2,059,075 (1936); (b) 2,066,925 (1937); (c) 2,110,412 (1938); (d) 2,123,492 (1938); (e) 2,140,194 (1938)—C.A. **31**, 247, 1039; **32**, 3420, 6667; **33**, 2696.
1746. D. L. Yabroff and A. C. Nixon, *Refiner Natural Gasoline Mfr.*, **19**, No. 3, 55-8 (1940); *Oil Gas J.*, **38**, No. 41, 74-6 (1940); *Natl. Petroleum News*, **32**, R56-62 (1940)—C.A. **34**, 3066.

1747. D. L. Yabroff and A. C. Nixon to Shell Dev. Co., U.S. pat. 2,228,041 (1941)—C.A. 35, 3075.
1748. D. L. Yabroff, E. L. Walters, A. C. Nixon, and H. B. Minor, (a) Natl. Petroleum News, 32, No. 50, R 445-8 (1940); (b) Oil Gas J., 39, No. 32, 35-6 (1940)—C.A. 35, 1611, 3071.
1749. D. L. Yabroff and E. R. White, Ind. Eng. Chem., 32, 950-3 (1940)—C.A. 34, 5640.
1750. D. L. Yabroff and E. R. White to N. V. Bataafsche, (a) Brit. pat. 503,644 (1939); (b) 522,450, 522,559 (1940); (c) 539,867 (1941); Dutch pat. 51,342 (1941); (d) Ger. pat. 726,680 (1942); (e) 735,327 (1943)—C.A. 33, 7546; 36, 1482, 4131; 37, 6277; 38, 4431.
1751. D. L. Yabroff and E. R. White to Shell Dev. Co., (a) U.S. pat. 2,149,379, 2,149,380 (1939); (b) 2,152,722 (1939); (c) 2,152,724 (1939); (d) 2,156,577 (1939); (e) 2,160,632 (1939)—C.A. 33, 4412, 5173, 5174, 6038, 7547.
1752. D. L. Yabroff and E. R. White to Shell Dev. Co., (a) U.S. pat. 2,164,851 (1939); (b) 2,168,851 (1939); 2,236,723 (1941); (c) 2,202,039 (1940); (d) 2,223,798 (1940); (e) 2,229,995 (1941)—C.A. 33, 8391, 9325; 35, 5302; 34, 7100; 35, 2313, 3429.
1753. D. L. Yabroff, E. R. White, and A. V. Caselli, Refiner Natural Gasoline Mfr., 18, 509-15 (1939)—C.A. 34, 1467.
1754. Teikichi Yamada, J. Soc. Chem. Ind. Japan, 40, Suppl. Bind. 44-7 (1937)—C.A. 31, 5635.
1755. M. P. Youker to Phillips Petroleum Co., U.S. pat. 2,048,241 (1936)—C.A. 30, 6184.
1756. D. W. Young to Jasco Inc., U.S. pat. 2,322,723 (1943)—C.A. 38, 212.
1757. E. G. Young, Soap Sanit. Chemicals, 23, No. 11, 116-7, 152A (1947)—C.A. 43, 9330.
1758. H. A. Young and M. B. Young, J. Am. Chem. Soc., 59, 811-2 (1937); *ibid.*, 60, 590-1 (1938)—C.A. 31, 4574; 32, 3331.
1759. H. W. Young and A. W. Peake, Chem. Met. Eng., 27, 972-6 (1922)—C.A. 17, 2638.
1760. M. B. Young and H. A. Young, J. Am. Chem. Soc., 64, 2282-7 (1942)—C.A. 36, 6880.
1761. M. A. Youtz and P. P. Perkins, (a) Ind. Eng. Chem., 19, 1247-50 (1927); (b) *ibid.*, 22, 610-1 (1930)—C.A. 22, 2266; 24, 3893.

- 1761.5. Yasuhide Yukawa and Yoshio Kishi, *Mem. Inst. Sci. Ind. Research, Osaka Univ.*, **8**, 163-7 (1951) (in English); *J. Chem. Soc. Japan, Pure Chem. Sect.*, **72**, 371-3 (1951)—C.A. **46**, 7061.
1762. Victor Zahn, *Anal. Chem.*, **9**, 543-7 (1937)—C.A. **32**, 453.
1763. E. V. Zappi and Pedro Egea, *Bull. soc. chim.*, [4] **51**, 748-51 (1932)—C.A. **26**, 5550.
1764. W. C. Zeise, (a) *Ann.*, **11**, 1-10 (1834); *Ann. chim. phys.*, [2] **56**, 87-96 (1834); (b) *Pogg. Ann.*, **31**, 369-431 (1834); *J. prakt. Chem.*, **1**, 257-68, 457-75 (1834); (c) *ibid.*, 345-56; (d) *ibid.*, 396-413.
1765. N. D. Zelinskii and Yu. K. Yur'ev, *Neftyanoe Khoz-yaistvo*, **26**, No. 9, 36 (1934); translation: *Foreign Petroleum Tech.*, **3**, 193-5 (1935)—C.A. **29**, 4927.
1766. T. Zerevitinov, *Ber.*, **41**, 2233-43 (1908)—C.A. **2**, 2810.
1767. W. T. Ziegenhain, (a) *Oil Gas J.*, **30**, No. 8, 29, 115 (1931); (b) *ibid.*, **40**, No. 16, 42, 46 (1941)—C.A. **25**, 5976; **35**, 8269.
1768. W. A. Zimmerscheid, R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner, *J. Am. Chem. Soc.*, **71**, 2947 (1949); *Ind. Eng. Chem.*, **42**, 1300-6 (1950)—C.A. **44**, 1033, 9356.
1769. Don Zimmet and J. P. Perrenoud, *Bull. soc. chim. biol.*, **18**, 1704-9 (1936)—C.A. **31**, 1729.
1770. T. Zincke and A. Dahm, *Ber.*, **45**, 3457-68 (1912)—C.A. **7**, 2392.
1771. T. Zincke and W. Frohneberg, (a) *Ber.*, **42**, 2721-36 (1909); (b) *ibid.*, **43**, 837-48 (1910)—C.A. **3**, 2577; **4**, 1746.
1772. T. Zincke and S. Lenhardt, *Ann.*, **400**, 1-27 (1913)—C.A. **7**, 3746.
1773. T. Zincke and J. Müller, *Ber.*, **46**, 775-86 (1913)—C.A. **7**, 1720-1.
1774. G. J. Ziser and J. H. Osmer to S. O. Co. of Calif., U.S. pat. 1,784,215 (1930)—C.A. **25**, 409.
1775. H. F. Zoller, *Ind. Eng. Chem.*, **15**, 845-7 (1923)—C.A. **17**, 2937.
1776. Paul Zurcher to Continental Oil Co., U.S. pat. 1,884,495 (1932)—C.A. **27**, 1158.

CHAPTER 3.

Negative Derivatives

General

The metal mercaptides are derivatives of mercaptans in which a positive metal has replaced the hydrogen of the sulfhydryl group. This chapter will be devoted to compounds in which the place of this hydrogen has been taken by a negative element or group. Some of these are well known and important, others much less so. Various types are presented here.

RSCI Sulphenylchloride	RSBr bromide	RSI iodide
RSOH Sulfenic acid	RSOR' ester	RSNH₂ amide
RSSH Thiosulfenic acid		RSSR' ester
RSCN Sulphenyl cyanide	RS·SCN thiocyanate	RS·SeCN selenocyanate
RSNO Alkyl thionitrite		RSNO₂ thionitrate
RS·COMe Ester of thioacetic		RS·CSMe of dithioacetic acid
RS·O·SR Sulfenic anhydride		RS·S·SR thioanhydride
(RS)₃P Trialkyl trithiophosphite	(RS)₃As trithioarsenite	(RS)₃Sb trithioantimonate
(RS)₃PO Trialkyl trithiophosphate		(RS)₃AsO trithioarsenate
(RS)₄C Tetraalkyl tetrathioorthocarbonate	(RS)₄Si silicate	(RS)₄Ge germanate
RS·SO₃Na Alkyl thiosulfate	RSO₂·SR' thiosulfonate	RSO·SR' thiosulfinate

Thiosulfenic esters, $RS\cdot SR'$, are alkyl disulfides and will be treated in a later chapter. Sulfenyl cyanides are thiocyanates in disguise and are so important that a whole chapter will be devoted to them in a later volume. The esters of thioacetic, and of other thio acids, are actually acyl derivatives of the mercaptans but, in conformity with long established usage, they are discussed in the chapter on thioacids. The same can be said for the dithio esters.

Sulfenic Acids and Derivatives

$RSOH$	RSX	$RSNR'R''$
Sulfenic acid	Sulfenyl halide	Sulfenamide
$RSOR'$		$(RS)_2O$
Sulfenic ester		anhydride

The stability of the inorganic and organic acids of sulfur goes down as there is less and less oxygen. ●

$O_2S(OH)_2$	$OS(OH)_2$	$S(OH)_2$
Sulfuric	Sulfurous	Sulfoxylic
$RSO_2\cdot OH$	$RSO\cdot OH$	$RS\cdot OH$
Sulfonic	Sulfinic	Sulfenic

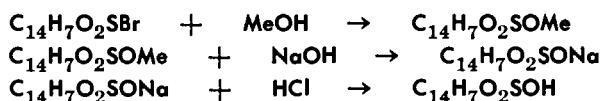
Alkyl and aryl sulfinic acids are unstable, the corresponding sulfenic acids are still less so; only one sulfenic acid is stable and can be isolated. It is α -anthraquinonesulfenic acid. Frequently the salts are stable while the free acids are not. There are only two stable sulfenic salts, the potassium salts of this acid and of its 4-amino substitution product.²⁵⁷ The corresponding α -anthraquinoneselenenic acid is also stable.^{70, 381a} The peculiar stability of these two acids has been attributed to some sort of ring formation involving the near-by carbonyl group.⁴⁵⁵ Hydrogen bonding has been advocated by some⁴¹⁷ and more extensive rearrangement by others⁴⁵⁵ to account for the stability of the salts.

The corresponding α -anthraquinoneselenenic acid has been made by treating the selenyl bromide with silver acetate. The *o*-nitro- and the 2,4-dinitrobenzeneselenenic acids have been prepared. The *p*-nitro- could be isolated only as the acetate. These develop color on the addition of alkali, which is attributed to salt formation. The salts are unstable.⁷⁰

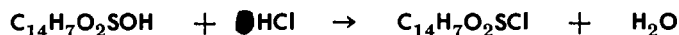
The acid halides, amides, esters, and anhydrides of the sulfenic acids are relatively stable and fairly well known. While,

with the one exception, the acids themselves cannot be isolated, it is often convenient to assume their transitory existence in explaining reactions.^{173, 261b, 263b, 370, 500} This subject has been ably reviewed.⁴¹⁷

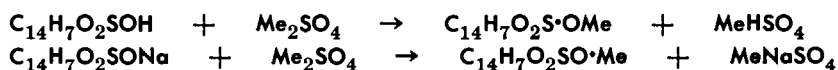
α -Anthraquinonesulfenyl bromide can be converted to the methyl ester by boiling it with methanol. When the ester is saponified and the hydrolyzate acidified, the anthraquinonesulfenic acid is precipitated as bright red crystals:



The free acid does not melt when heated, but gives off water and passes into the anhydride. With hydrogen chloride, or bromide, it goes back to the halide:

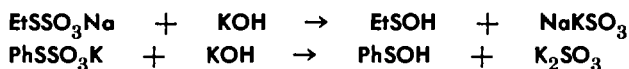


The acid dissolves in aqueous alkali. The aqueous solutions of the sodium and potassium salts are blue, but alcoholic solutions are green. If protected from the air, these solutions remain unaltered but are oxidised by air to the sulfinates.²⁵⁷ The free acid is converted by methyl sulfate to its methyl ester, but with the same reagent its sodium salt goes to the isomeric methyl α -anthraquinone sulfoxide:^{260b}

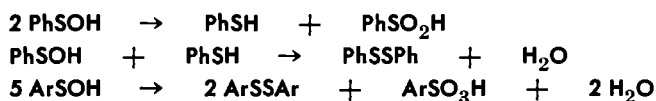


This is analogous to the formation of a sulfone from a sodium sulfinite.

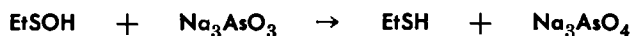
The alkaline hydrolysis of an alkyl or aryl thiosulfate is believed to give a sulfenic acid:^{190, 317a, 317b}



While only the α -anthraquinonesulfenic acid can be isolated,^{190, 612a} it is convenient to write equations involving the assumed sulfenic acid to account for the end products which are obtained. Thus disproportionation may take place:^{190, 444}



The sulfenic acid is an oxidising agent: ^{317a, 317b}



The hydrolysis of a disulfide is also assumed to give a sulfenic acid: ^{572, 623, 627, 628, 630}



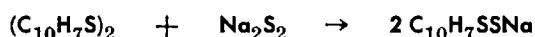
This will be discussed more fully in the chapter on disulfides. It has been suggested that a sulfenic acid may result from the disproportionation of a sulfinic: ^{263a, 350a}



It may be an intermediate in the reduction of a sulfone chloride to the mercaptan.⁷⁵⁵

There is good evidence that cysteine is oxidised by permonosulfuric acid to the sulfenic acid, $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{SOH}$.⁷⁰³

β -Naphthyl disulfide dissolves in an aqueous solution of sodium disulfide:



Acidification gives the thiosulfenic acid, $\text{C}_{10}\text{H}_7\text{SSH}$.⁷³³ Thiosulfenic acids, RSSH , have been postulated as intermediates.^{193, 318a}

SULFENYL HALIDES, RSX

Formation

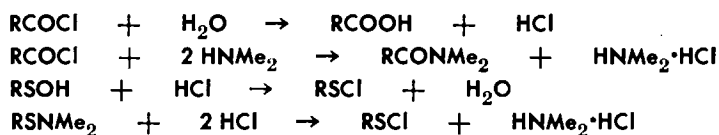
The halogen derivatives are called sulfenyl halides to show their relation to the sulfenic acids:



Formally this relation is the same as between acid halides and carboxylic acids:



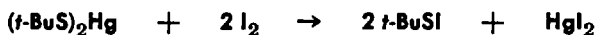
Here, however, the usual relationships are reversed; the sulfenyl chlorides are much better known and easier to prepare than the corresponding sulfenic acids. Typical acid chloride reactions may be reversed:



In the order of importance the sulfenyl halides are: the chlorides, RSCl , the bromides, RSBr , and the iodides, RSI . So far no fluorides, RSF , have been prepared.

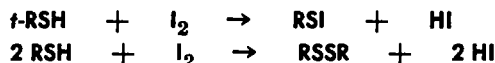
In the fluorination of methyl mercaptan, the compound, F_3CSF , is probably formed, but the tendency of sulfur to take on more fluorine is so strong that the only thing that can be isolated is F_3CSF_5 , $m.-86.9$, $b.-20.4^\circ$.⁶⁴⁶ Its breakdown potential has been measured.²⁷⁶ The fluorination of carbon disulfide gives a number of products, F_3CSF_5 , $b.-21^\circ$; F_3CSF_3 , $m.-110^\circ$, $b.-7^\circ$; SCF_2 , $m.-134^\circ$, $b.-46^\circ$; $\text{F}_2\text{C}(\text{SF}_3)_2$, $m.-51^\circ$, $b.26^\circ$; $\text{F}_3\text{SCF}_2\text{SF}_5$, $m.-70^\circ$, $b.62^\circ$.⁷¹⁶ The chlorination of mercury trifluoromethyl mercaptide, $(\text{F}_3\text{CS})_2\text{Hg}$, leads to $(\text{F}_3\text{CS})_2$ and F_3CSCl , $b.-0.7^\circ$,³³³ which is analogous to perchloromethyl mercaptan which will be taken up later in this chapter.

When *t*-butyl mercaptan vapor, diluted with an inert gas, is passed through an alkaline hypochlorite solution, the sulfenyl chloride, *t*-BuSCl, is formed.⁶³⁶ This is formed also when chlorine is passed into a hydrocarbon solution of the disulfide at -40° .^{349a} An ether solution of the iodide, *t*-BuSI, can be prepared by adding iodine to a suspension of the mercury mercaptide in cold ether:



The deep orange-red ether solution is stable for some time if kept cold.^{590b, 595}

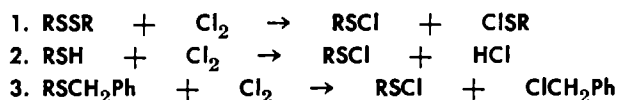
In the amperometric titration of a mercaptan with iodine, twice as much iodine is used up by a tertiary mercaptan as by a primary:⁴³⁷



Cysteine, though not a tertiary mercaptan, reacts in this way.

Methanesulfenyl iodide, MeSI , has been assumed to be an intermediate product in the production of methyl sulfide and trimethylsulfonium triiodide from methyl disulfide and methyl iodide.⁶⁷⁶

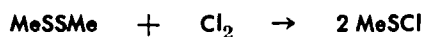
The sulfenyl chlorides, RSCl , will be considered first. The same methods are used for the bromides, RSBr , and iodides, RSI , if they can be made to work. There are three general and several special methods. The chief ones involve chlorinolysis:



The limitation of these is the readiness with which the group R is chlorinated. Benzenesulfonyl chloride, PhSOCl , can be made by chlorinating diphenyl disulfide. If, however, the benzene ring contains a group, such as the amino or hydroxyl, substitution will take precedence over chlorinolysis. Or, to look at it the other way, if a sulfonyl chloride is formed, the chlorine will migrate into the ring. However, a nitro, or a carbonyl, group, protects the ring against substitution and favors the formation of a stable sulfonyl halide. As a matter of fact, the anthraquinone and the nitro- and dinitro-benzene sulfonyl halides are the ones that are the most easily prepared and are the most stable. Aliphatic radicals also are subject to halogenation, so that conditions which favor it must be avoided.

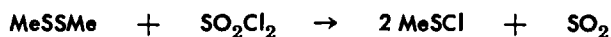
Since the sulfonyl halides are reactive, they must be prepared in dry, nonpolar solvents, such as chloroform, carbon tetrachloride, or benzene.

Methanesulfonyl chloride is formed when the calculated amount of dry chlorine is passed into methyl disulfide at -20° :^{93, 100}

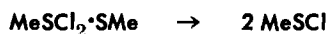


The ethyl, propyl, *i*-propyl, and butyl compounds have been made similarly.⁹⁷

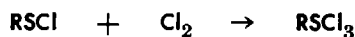
Sulfonyl chloride may be the chlorinating agent:¹⁰⁰



Methyl sulfonyl chloride boils at $27-8^\circ$ under 50–60 mm. pressure. With additional chlorine,^{93, 100} or with sulfonyl chloride,⁹⁶ at a slightly higher temperature, substitution takes place and the product is ClCH_2SOCl , $b_{12} 123^\circ$, $d_{20} 1.526$.^{93, 100} According to another author, chlorination at -15° gives $\text{MeSOCl}_2\cdot\text{SMe}$ which, on warming to room temperature, goes into the sulfonyl chloride:



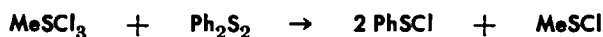
The sulfonyl chloride, $b_{60} 20-3^\circ$, when kept in sunlight, chlorinates itself to ClCH_2SOCl , $b_{12} 25^\circ$.⁶²⁶ The chlorination of the sulfonyl chloride has been formulated as going in two steps:



The trichloride is stable only at low temperatures. The chlorine migrates to the alkyl: ^{109, 194}

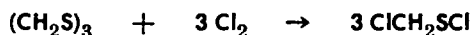


An alkyl sulfur trichloride may act as a chlorinating agent: ¹⁰⁹



Continued chlorination gives Cl_2CHSCl and Cl_3CSCl .¹⁹⁷

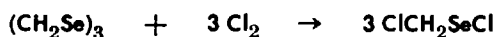
The initial product in the chlorination of trithiane is chloromethyl sulfenyl chloride:



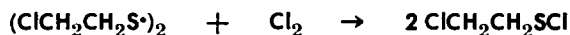
The homologs of trithiane react similarly.¹⁹⁶ ClCH_2SCl , b_{18} 33° , n 20/D 1.542, d 0/4 1.55, d 20/4 1.52. MeCHClSCl , b_{40} $47-50^\circ$, n 20/D 1.5102, d 0/4 1.363, d 20/4 1.347. EtCHClSCl , b_{27} $62-4^\circ$, n 20/D 1.501, d 0/4 1.301, d 20/4 1.276. PrCHClSCl , b_{15} $62-5^\circ$, n 20/D 1.490, d 20/4 1.202. Me_2CClSCl , b_{26} 40° , n 20/D 1.493, d 0/4 1.273, d 20/4 1.493.

Under different conditions, the chlorination may go further and produce dichloromethanesulfenyl chloride, Cl_2CHSCl . This is a yellowish-red fuming liquid, d_{34} 1.6143, n 34/D 1.5428. One of the chlorines attached to the carbon, as well as the one on the sulfur, is active.⁷⁴⁸ Other data for ClCH_2SCl are: b_{100} 64° , d 26/4 1.5613, n 26/D 1.5434.¹⁹⁹ Divergencies in data for unstable compounds are to be expected. The fully chlorinated compound, Cl_3CSCl , known as perchlormercaptan, will be discussed in a later section. When trithiane is chlorinated in acetic acid, the sulfonyl chloride, $\text{ClCH}_2\text{SO}_2\text{Cl}$, is formed.⁹⁶ Ethyl disulfide and sulfuryl chloride give the α -chloroethanesulfenyl chloride, MeCHClSCl .⁹⁴

The chlorination of triselenane gives chloromethylselenenyl chloride: ⁹²



2-Chlorethylsulfenyl chloride, $\text{ClCH}_2\text{CH}_2\text{SCl}$, b_{15} $47-7.5^\circ$, is obtained by passing chlorine into a cold solution of 2-chloroethyl disulfide in carbon tetrachloride: ^{267, 495}

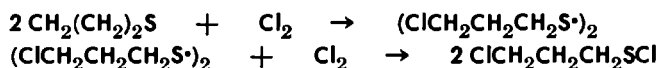


This, the key intermediate in the formation of mustard gas from ethylene and sulfur chloride, will be treated in the chapter on substituted sulfides. The 2-chloro-1-methylethylsulfenyl chlo-

ride, $\text{ClCH}_2\text{CHMeSCl}$, has been made by chlorinating the corresponding disulfide in dry chloroform.⁶⁸¹

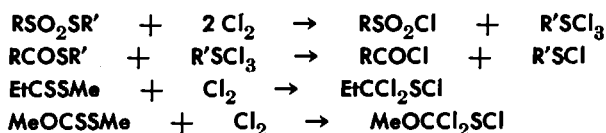
By the use of a mild chlorinating agent, such as N-chlorosuccinimide, ethyl thioglycolate has been converted to the sulfenyl chloride, $\text{ClSCH}_2\text{CO}_2\text{Et}$.²²³

In the chlorination of trimethylene sulfide the first product is the 3-chlorodisulfide which goes into the sulfenyl chloride: ⁶⁸⁰



The double sulfenyl chlorides, $\text{ClS}(\text{CH}_2)_3\text{SCl}$ and $\text{ClS}(\text{CH}_2)_4\text{SCl}$, have been made by chlorinating the corresponding cyclic disulfides.⁹⁸

Several reactions take place when a thiolester is chlorinated. Sulfenyl chlorides are among the products. A thionyl sulfur is replaced by chlorine.¹⁹⁸



Treating a malonamide or a methylmalonamide with sulfur dichloride replaces the active hydrogen by $-\text{SCl}$. The products are $(\text{RNHCO})_2\text{C}(\text{SCl})_2$ and $(\text{RNHCO})_2\text{CMeSCl}$.⁵²⁸

Aralkyl compounds are known: ¹⁹⁸ $\text{PhCHCl}\cdot\text{SCl}$, b_{10} 82° , $d_{20/4}$ 1.2485, $d_{0/4}$ 1.2691, $n_{20/D}$ 1.5507; $\text{PhCMeCl}\cdot\text{SCl}$, b_{11} $87-8^\circ$, $d_{0/4}$ 1.2339, $d_{20/4}$ 1.2173, $n_{20/D}$ 1.5432.

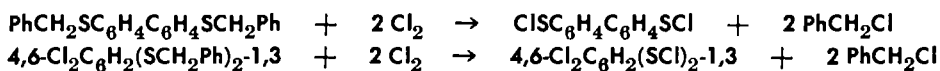
The aromatic sulfenyl chlorides are even better known than the aliphatic. Phenyl mercaptan can be chlorinated to phenylsulfenyl chloride, PhSCl .⁴⁵⁷ If chlorine is passed into the carbon tetrachloride solution of the mercaptan in a freezing mixture, the product is phenyl sulfenyl chloride,⁴⁵⁶ but if it is cooled only to 0° it is *p*-chlorophenylsulfenyl chloride.²⁷⁷ This can be obtained also by chlorinating *p*-chlorothiophenol.⁶⁶⁷ β -Naphthyl mercaptan gives β -naphthylsulfenyl chloride or its chlorination product, according to conditions.⁷⁵⁸ *p*-Acetylaminothiophenol, in which the amino group is protected by acetylation, can be converted to the sulfenyl chloride by this method.⁷⁶⁴ Thiosalicylic acid has been chlorinated to the sulfenyl chloride. The carboxyl group hinders substitution.³³¹ *m*-Dimercaptobenzene is chlorinated to the dichlorodisulfenyl chloride, $\text{Cl}_2\text{C}_6\text{H}_2(\text{SCl})_2$.⁷⁶¹

4,4'-Dimercaptodiphenyl gives the corresponding disulfenyl chloride, $\text{ClSC}_6\text{H}_4\text{C}_6\text{H}_4\text{SCl}$.^{754, 757} 1-Fluorenonethiol can be chlorinated to the sulfenyl chloride.⁴⁰⁹

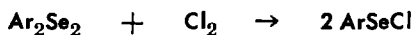
The *p*-benzene sulfenyl-sulfonyl chloride, $\text{ClSC}_6\text{H}_4\text{SO}_2\text{Cl}$, has been made by the reaction of chlorine with the disulfide.⁷²⁴ The sulfonyl group protects the ring from chlorination. Of all the sulfenyl halides, the nitroaromatic are the easiest to prepare and handle. The nitro group protects the ring from chlorination, both during the preparation and subsequently. *o*-Nitrobenzene sulfenyl chloride, $\text{NO}_2\text{C}_6\text{H}_4\text{SCl}$, melts at 75° ,^{385, 480} the corresponding *para* compound at 52° ,⁷⁶² the *o*-nitro-*p*-methyl- at 90° ,⁷⁶³ and the 2,4-dinitro- at 96° .⁴¹⁰ All of these are conveniently prepared by the action of chlorine on the disulfides. The 2,4-dinitro-sulfenylchloride is used as a reagent. The method of preparing it and the corresponding bromide have been fully described^{55, 258, 414, 418, 561} and the hazards in making and handling it have been pointed out.⁴⁰⁷ The *m*-nitrobenzenesulfenyl chloride is too unstable to be isolated but can be used in synthesis.^{248, 455} The 2,5-dichlorobenzenesulfenyl chloride,^{277, 517} m. 33° ,⁵¹⁷ the less stable 2,5-dibromo-,⁶⁷⁹ and the two stable anthraquinonesulfenyl chlorides, α - m. 224° ²⁵⁷ and β - m. 136° ,^{260b} have been prepared similarly.

Triphenylmethylsulfenyl chloride, m. 137° , has been made by treating the mercaptan with sulfuryl chloride, which is a chlorine donor.⁷²⁰

A benzyl sulfide may be cleaved by chlorine: ^{754, 757}

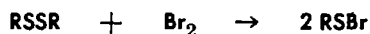


Treating an aryl diselenide with chlorine⁷⁰ or with sulfuryl chloride^{70, 71} gives an aryl selenenyl chloride:



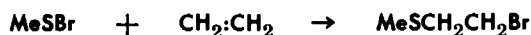
Under the same treatment, the aryl diselenide-sulfide, $(\text{ArSe})_2\text{S}$, gives the same result.^{592a}

The addition of bromine to a disulfide dissolved in chloroform, or carbon tetrachloride, gives a sulfenyl bromide:



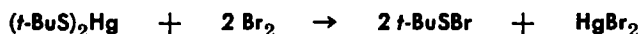
The isolation of the sulfenyl bromide is not always easy and may not be necessary. Thus when ethylene is passed into a carbon

tetrachloride solution of methyl mercaptan and bromine at -20° , the product is $\text{MeSCH}_2\text{CH}_2\text{Br}$. This must have been formed from the sulfenyl bromide: ⁶²⁶

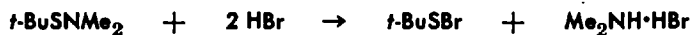


The first attempt to prepare the benzene derivative did not succeed, ^{547a} but subsequently it was obtained in solution. ⁴⁵⁷ The *p*-acetamino- ¹³⁹ and the 2,5-dibromo- ⁵¹⁷ compounds have been obtained in solution and used in syntheses. The 2-nitro-4-chloro compound, $m.111^{\circ}$, ⁷⁵⁶ and the 2-nitro-5-methyl compound, $m.84^{\circ}$, ^{249b} are stable and so is the 2-benzoyl-4-nitro-. ²⁵⁹ The α -anthraquinonesulfenyl bromide, $m.214^{\circ}$, is the most stable of this class. ²⁵⁷ Its 4-amino derivative has been obtained only as the hydrobromide. ^{260c}

A mercury mercaptide reacts with bromine:



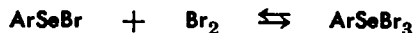
The same product is obtained when the sulfenamide is cleaved by hydrogen bromide: ^{593c}



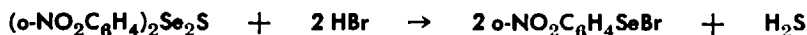
The sulfenyl chloride results with hydrogen chloride. ^{593c} Benzenesulfenyl chloride has been made by this method. ⁴⁵⁶

α -Anthraquinonesulfenyl bromide can be prepared by the reduction of the sulfinic acid with hydrogen bromide. ^{260a} 1-Fluorenesulfenyl bromide has been made by brominating the thiol. ⁴⁰⁹

An aryl selenenyl bromide can be made by treating an aryl selenocyanate, ArSeCN , diselenide, triselenide ⁷¹ or diselenosulfide ^{592d} with bromine. The selenium may take up additional bromine, forming the tribromide. This is in equilibrium with the monobromide:



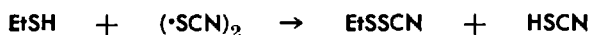
This shifts to the left as the temperature is raised. ⁶⁹ *o*-Nitrophenyl diselenide-sulfide is cleaved by hydrobromic acid: ^{592d}



Usually the iodides are unstable, but 2-benzothiazolesulfenyl iodide has been prepared, like the bromide and chloride, by the addition of the halogen to a solution of the disulfide. ^{218, 506}

Sulfenyl Thiocyanates, RS·SCN

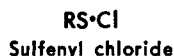
The fact that thiocyanogen ($\cdot\text{SCN}$)₂ resembles a halogen in many of its reactions suggested trying it with a mercaptan. It does react:



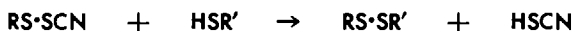
The product is a sulfenyl thiocyanate.^{369, 460a, 461, 595} If thiocyanogen were more available, this would be a desirable method since it is not as active in substitution as the halogens.

Only a few of these sulfenyl thiocyanates have been prepared: PhSSCN, low melting crystals;^{456, 461} EtSSCN, b_{1.5} 52°;⁴⁶¹ 2-O₂NC₆H₄SSCN, m. 94°;^{460, 461} 2,4-(O₂N)₂C₆H₄SSCN, m. 84°;⁸¹⁴ β-C₁₀H₇SSCN, m. 75°.^{461, 470}

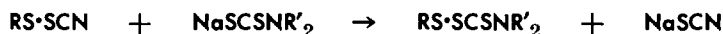
In physical and chemical properties, the sulfenyl thiocyanates resemble the sulfenyl halides. If thiocyanogen is a pseudohalogen, this is as it should be.



They react with mercaptans to form disulfides:^{460a, 461}



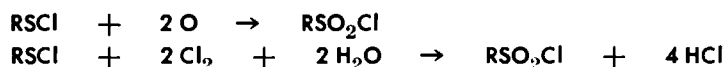
The analogous formation of the ester, RSOR', will be considered later. The reaction with a dithiocarbamate is similar:³⁶⁹

*Reactions*

2,4-Dinitrobenzenesulfene chloride gives a colored ion in 100% sulfuric acid.⁴¹¹

Oxidation and Reduction

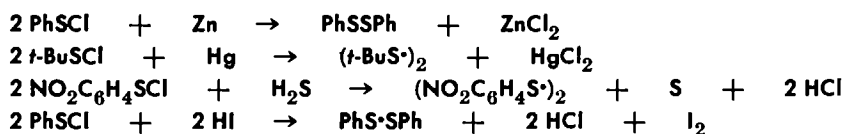
A sulfenyl chloride is oxidised by nitric acid,^{97, 757, 758, 759, 762} or by chlorine in acetic acid,^{1, 409, 711, 757, 760b, 763} to the sulfone chloride:



It is possible that sulfenyl chloride is an intermediate in the well-known oxidation of a mercaptan or a disulfide to the

sulfonyl chloride by chlorine in cold water. At -20° nitric acid oxidises methanesulphenyl chloride to the thiolsulfonate, MeSO_2SMe .⁹⁷ A sulphenyl bromide, in acetic acid, is oxidised by bromine to the sulfonyl bromide.^{760a} The oxidation can be effected by air containing oxides of nitrogen.⁵⁷⁸

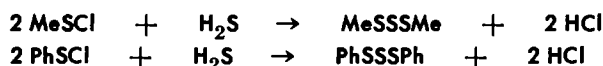
Sulphenyl chlorides are reduced readily to the disulfides:



Zinc,⁴⁵⁶ mercury,^{101, 590b, 595} potassium hydrosulfide,¹⁹³ iodide ions,^{82, 672} or sodium thiosulfate⁷⁰² may be the reducing agents. Lithium aluminum hydride is effective.⁶⁸⁴ Benzene-selenenyl bromide is reduced by zinc to phenyl diselenide.⁷¹

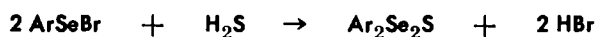
With Hydrogen Sulfide and Mercaptans

With hydrogen sulfide the product may be a trisulfide:^{97, 329, 454b}

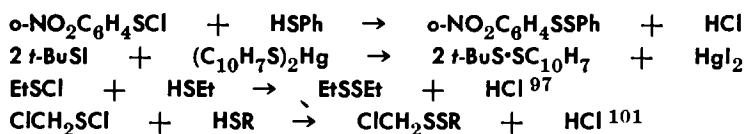


Disulfides and tetrasulfides are formed along with the trisulfide.⁹⁷ 1,4-Butanedisulphenyl chloride, $\text{ClS}(\text{CH}_2)_4\text{SCl}$, and dry halogen sulfide give polymeric tetramethylene trisulfide.⁹⁸

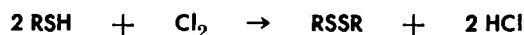
An aryl selenenyl chloride, bromide, thiocyanate, or selenocyanate and hydrogen sulfide give the diseleno-sulfide:^{592a}



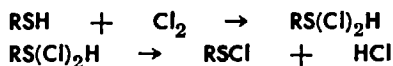
A sulphenyl chloride reacts with a mercaptan, or a mercaptide, to give disulfide: ^{101, 197, 454a, 456, 590b, 595, 696, 720}



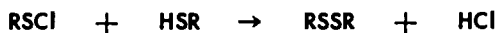
The sulphenyl chloride may be assumed to be an intermediate in the conversion of a mercaptan to a disulfide by treatment with a halogen. The over-all reaction is written:



The halogen certainly does not react simultaneously with two molecules of a mercaptan. It is more likely that it adds to the sulfur atom of one:

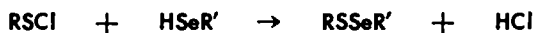


The sulfonium type complex would lose hydrogen chloride and the sulfenyl chloride would react with the second molecule of mercaptan:



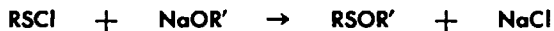
As shown in the equations above, the reaction of a sulfenyl chloride with a mercaptan is a method of preparing unsymmetrical disulfides. Starting with stable sulfenyl chloride, such as that of 2,4-dinitrobenzene, unsymmetrical disulfides, 2,4-(NO₂)₂-C₆H₃SSR, may be prepared. Some of these may serve for the identification of the mercaptans.

The reaction with a selenomercaptan is similar: ^{592c}



With Metallic Salts

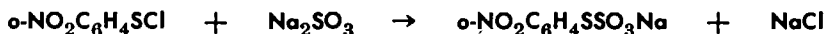
With a sodium alcoholate or phenolate sulfenic esters are formed:



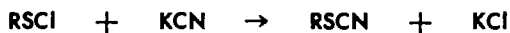
This will be treated later as a preparation method. A silver salt of a sulfinic acid gives a thiosulfonic ester: ^{260a, 291, 457, 517, 759}



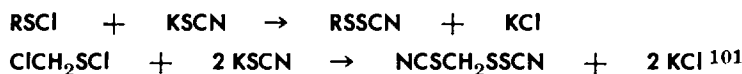
As stated in the section on thiosulfonic esters, this reaction was used to settle the question of their constitution.⁵¹⁷ A sulfenyl chloride and sodium sulfite give the thiosulfate: ⁴⁵⁵



With potassium cyanide in acetic acid, a thiocyanate is formed: ^{97, 101, 756, 758, 759, 762, 763}

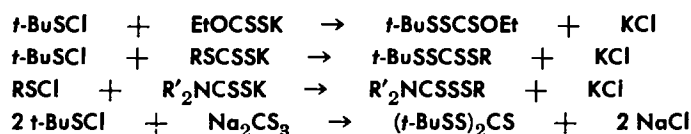


With metal thiocyanates sulfenyl thiocyanates are produced: ^{249b, 340b, 418, 456, 400a, 595}



Selenium compounds, ArSSeCN , ArSeSCN and ArSeSeCN have been prepared similarly.^{71, 249a, 592a, 592b, 596}

Sulfenyl halides react with xanthates, thioxanthates,^{349d} dithiocarbamates,^{302, 303} and trithiocarbonates:³²

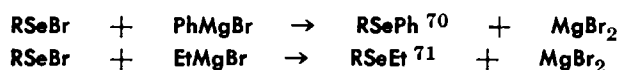


A sulfide is produced when a sulfenyl halide reacts with the sodium salt of a nitroparaffin. The RS- is attached directly to the carbon chain. The product from nitroethane is $2,4\text{-(O}_2\text{N)}_2\text{-C}_6\text{H}_3\text{SCH(NO}_2\text{)Me}$.⁴¹³

As both of the chlorine atoms in chloromethanesulfenyl chloride are active, it reacts with two molecules of a Grignard reagent:¹⁰¹



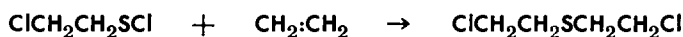
The reaction of a selenenyl bromide with a Grignard reagent is similar to that of the sulfenyl halide:



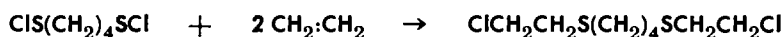
Compounds, such as RSeSPO(OMe)_2 , $\text{RSeS}_2\text{O}_2\text{Me}$, RSeSO_2Ph , and $\text{RSeS}_2\text{O}_3\text{K}$, have been made from a selenenyl bromide with di-O-alkylmonothio phosphates, thiosulfenates, and thiosulfates.^{249a}

Addition to Unsaturation

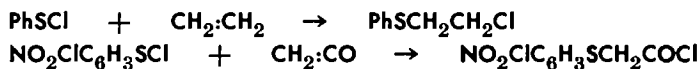
The formation of mustard gas has been shown to involve the addition of a sulfenyl chloride to ethylene:²⁶⁷



This will be discussed when mustard gas is considered in the chapter on substituted sulfides. Methane- and ethane-sulfenyl chlorides have been added to styrene, cyclohexene, and cyclooctatetrene.⁹⁷ Chloromethanesulfenyl chloride has been added to unsaturates.¹⁰¹ Two molecules of ethylene combine with 1,4-butanedisulfenyl chloride:⁹⁸



Benzene-, *p*-toluene-, 2-nitrobenzene-, 2,4-nitrochloro-, and 2,4-dinitrobenzene-sulfonyl chlorides have been added to unsaturated hydrocarbons^{163, 410, 412, 415, 418, 457, 714} and 2,4-nitro-chloro-benzene sulfonyl chloride to ketene:⁶⁰⁴



Sulfonyl halides have been added to vinyl acetate:³⁷⁶



α -Anthraquinonesulfonyl bromide has been added to cyclohexene.^{381b} A kinetic study has been made of the addition of 2,4-dinitrobenzenesulfonyl chloride to styrene.⁵⁴⁴ This sulfonyl chloride has been added to acetylene and to dimethyl- and diethyl-acetylenes:

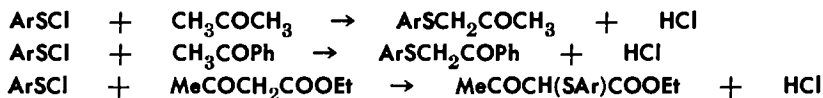


The product melts at 130.5°. The compounds from the two substituted acetylenes melt at 76° and 66°.⁴⁰⁸

Addition to unsaturates is a general reaction of alkanesulfonyl chlorides.⁹⁹ They are even more reactive than the aromatic but, as they have become available only recently, fewer examples of their use are to be found in the literature. Chloromethanesulfonyl chloride has been added to ethylene¹⁹⁷ and to acetylene.¹⁰²

Miscellaneous

Aromatic sulfonyl chlorides react with acetone, acetophenone, acetoacetic ester, and with other compounds in which there is an active hydrogen: 99, 280b, 754, 756, 759, 762, 763, 764



The corresponding sulfonyl bromides do not react as regularly as the chlorides.⁷⁶³

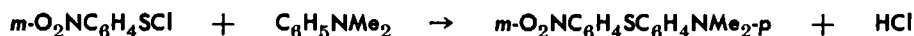
Less is known about the reactions of the alkanesulfonyl chlorides, since they have become available only recently. Methanesulfonyl chloride and cyclohexanone give 2-methylmercaptocyclohexanone. Ethane sulfonyl chloride and acetoacetic ester give the α,α -diethylmercapto ester, $\text{MeCOC(SEt)}_2\text{CO}_2\text{Et}$. Only one

alkylmercapto group enters malonic ester.⁹⁷ A cyclic compound is obtained when chloromethanesulfonyl chloride reacts with sodium acetoacetic ester.¹⁰¹ Macromolecular resins may be formed from chloroalkanesulfonyl chlorides and cyclohexanone.⁹⁵

Substitution of the RS- group in an aromatic takes place where an activating group, such as hydroxyl or amino, is present. Phenol, *ortho*- and *meta*-cresols, resorcinol, catechol, thymol and the naphthols react readily with sulfonyl chlorides to give hydroxy sulfides.^{247, 248, 257, 403, 453, 457, 679, 724, 759, 762, 763} The substitution is normally in the para position. Nearly all of these reactions have been carried out with the nitro-substituted benzenesulfonyl chlorides on account of their availability and stability. Recently considerable work has been done with alkanesulfonyl chlorides. Macromolecular resins may be obtained with phenols.⁹⁵ In the absence of an activating group, such as hydroxyl, a catalyst, such as aluminum chloride, has to be used.^{114, 260b, 457, 720} Methyl phenyl sulfide, MeSPh, has been prepared from methanesulfonyl chloride and benzene in the presence of aluminum chloride.⁹⁷

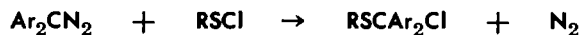
With a primary amine, the first product is probably a sulfenamide which rearranges to the amine sulfide. If the reaction is carried out at low temperatures, the sulfenamide may be isolated, but at higher, the amine sulfide is obtained directly.^{260b, 759, 763}

The ArS- group is substituted for a hydrogen of dimethyl aniline by treating it with a sulfonyl halide: ⁴⁵⁵



The reaction of α -anthraquinoneselenenyl bromide is similar.⁷⁰

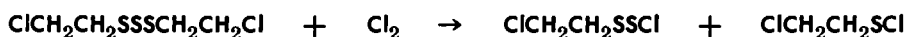
Aromatic sulfonyl chlorides react smoothly with diazomethane and its diaryl derivatives: ^{631, 632}



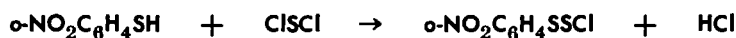
DISULFIDE CHLORIDES, RSSCl AND ArSSCl

Only a few compounds of this class have been prepared. Anthracene and sulfur monochloride give 9-C₁₄H₉SSCl.^{255, 470.5} The reaction is rapid with crude anthracene, but slow with the purified.⁷⁴⁷ A dye from this has been claimed.¹³¹ In the presence of a mercury-aluminum couple, two such groups are introduced and the product is 9,10-C₁₄H₈(SSCl)₂. Naphthalene gives α -C₁₀H₇-

SSCl^4 The chlorination of 2,2'-dichloroethyl trisulfide gives a mixture of two chlorides: ²⁸⁶



o-Nitrothiophenol and sulfur dichloride give the *o*-nitrophenyl disulfide chloride: ^{329, 460b}

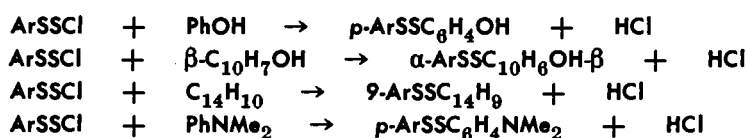


This is a relatively stable compound which can be kept for some time in a desiccator at room temperature. ³²⁹

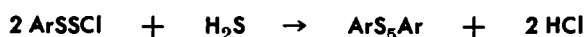
The reactions of disulfide chlorides have been studied using the before-mentioned *o*-nitrophenyl disulfide chloride, which for simplicity will be written ArSSCl .

Addition to unsaturates takes place: to olefins, cyclohexene, stilbene, 1,1-diphenylethylene and ketene. ³²⁹

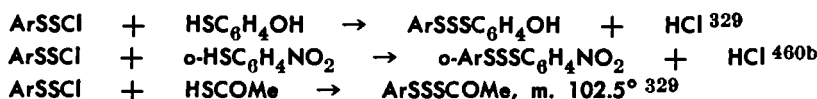
The ArSS- group can be substituted for an active hydrogen in ketones, acetone, acetophenone or acetoacetic ester or in aromatics, such as phenol, β -naphthol, anthracene or dimethylaniline: ³²⁹



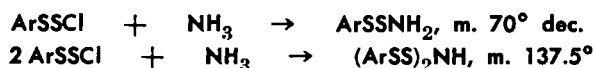
With hydrogen sulfide a pentasulfide is formed: ³²⁹



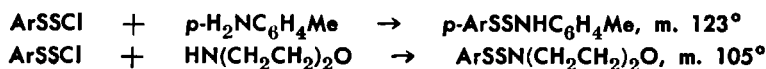
Mercaptans give trisulfides:



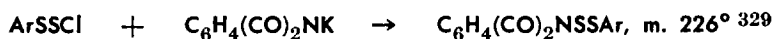
According to conditions, two different products may be obtained from ammonia:



p-Toluidine and morpholine react similarly:

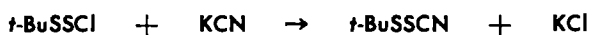


There is no reaction with phthalimide, but there is with its potassium derivative:



With silver *p*-toluenesulfinate the product is *p*-MeC₆H₄SO₂SSAr, m. 142°. ³²⁹

With potassium cyanide a part of the sulfur went to form potassium thiocyanate leaving the arylthiocyanate, ArSCN. ³²⁹ This transfer of sulfur did not take place with the *t*-butyl chloride: ^{349b}



This chloride gave a trithiocarbamate, *t*-BuSSCSNR₂. ^{349c}

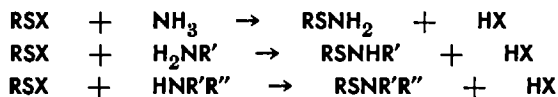
Similar reactions have been carried out, using anthracenedithiochloride with ammonia and with an amine. ²⁵⁵

SULFENAMIDES, RSNH₂, RSNHR', RSNR'R''

Formation

These have an amino, or substituted amino group, for the hydroxyl of the sulfenic acid, RSOH. They are by far the largest class in the sulfenic group. They outnumber the sulfenyl halides since several amides can be made from each halide. Finding industrial uses for some of them has stimulated the preparation of others. Several other ways of making them have been devised.

The most direct method is still the reaction of a sulfenyl halide with ammonia or an amine:



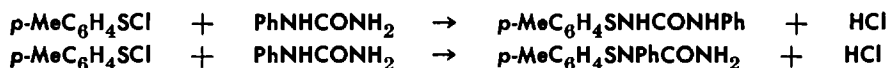
This is analogous to the preparation of amides from acid chlorides, but a sulfenyl chloride can go further, to the imide. A substituted urea reacts as an amine.

In preparing a sulfenamide, ammonia, or an amine, is added to the sulfenyl halide dissolved in ether or other nonpolar solvent. The hydrogen halide is taken care of by an excess of the amine. The reactions usually go spontaneously, even at low temperatures. The yields are generally high. Weakly basic amines do not react so well,⁷⁷ but derivatives from them may be obtained at higher temperatures.²⁸⁰

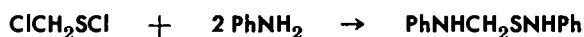
Sulfenamides have been prepared by this method from a number of sulfenyl chlorides, from butane-,⁵⁶⁴ from trimethyl-^{349a, 564, 590b, 593c} and triphenyl-methane-,⁷²⁰ from 4-acetylamino benzene-,^{493, 504} from 4-amino-1-anthraquinone-,^{260c} from α - and β -anthraquinone-,^{260b} from benzene-,^{457, 493, 506} from 4-chloro-2-nitrobenzene-,^{277, 278, 279, 280, 281, 520b, 756} from *p*-chlorobenzene-,⁴⁹³ from 2,5-dichlorobenzene-,²⁷⁷ from 4-methyl-2-nitrobenzene-sulfenyl chloride,⁷⁶³ and from others.^{249b, 259, 457, 458, 752} *m*-Nitrobenzene-sulfenyl chloride reacts with dialkylamines.⁴⁵⁵ *o*-Nitrobenzene-sulfenyl bromide has been caused to react with esters of several amino acids²²² and the *para* chloride with various heterocyclic amines.^{57, 504} A sulfenamide may be made from an amine and a sulfenyl thiocyanate: ^{456, 460a, 751}



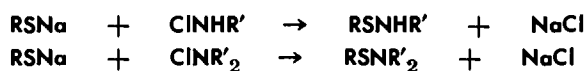
p-Toluenesulfenyl chloride may react with either end of phenyl-urea: ⁴⁴⁴



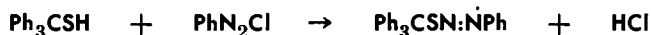
Chloromethanesulfenyl chloride reacts with two molecules of aniline: ¹⁰¹



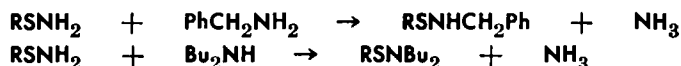
Sulfenamides may be made, the other way around, by the reaction of a chloroamine on a mercaptide: ^{7, 310, 373}



A diazoamide has been made from benzenediazonium chloride and triphenylmethyl mercaptan: ⁷²⁰

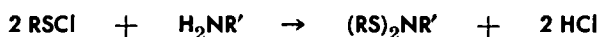


An amine displaces ammonia from a sulfenamide: ^{364, 712}

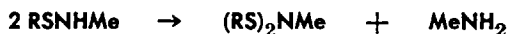


This is a convenient synthesis for certain compounds.

If an excess of the sulfenyl chloride is used with ammonia or with a primary amine, the result is an imide: ^{457, 756, 758}



When a sulfenamide is boiled with acetic acid, half of the ammonia, or amine, is split out and an imide is left:



Those that have been reported are aromatic and are solids with rather high melting points. Properties of some of these are in Table 1.3.

When a 1% solution of the benzenesulfenimide, $(\text{PhS})_2\text{NH}$, in ether is shaken with lead peroxide and potassium carbonate, the solution takes on a violet color which deepens on dilution. Evaporation of the ether leaves colorless crystals which give a violet solution. The white crystals are supposed to be $(\text{PhS})_2\text{N}\cdot\text{N}(\text{SPh})_2$ which dissociates in solution into colored free radicals. The same phenomena are observed with the *o*-nitro derivative.⁴⁵⁸

An entirely different method of making sulfenamides is the oxidation of a mixture of an amine and a mercaptan:



Nothing appears to be known about the mechanism of the reaction, or reactions, but good results are claimed. Various oxidising agents are recommended, hypochlorites, persulfates, ferricyanides, hydrogen peroxide, and halogens. This method has been exploited extensively and many modifications of it have been patented.^{7, 35, 126, 151, 157, 325, 327, 372, 519, 636, 660, 712, 752}

Selenenamides have been prepared.¹⁵⁶

Properties of Sulfenamides

The sulfenamides are by far the most stable and the best-characterized compounds in the sulfene group. Except for some of low molecular weight, they are solids with sharp melting points. The 2-nitro- and 2,4-dinitro-benzene compounds have proved to be useful for the identification of amines. A number of these are in Table 1.3 along with some 2,4-nitrochloro compounds.

Reactions

The sulfenamides do not have the acidic properties of the sulfonamides.⁷⁷ They differ from other classes of amides in their ease of acylation. Their acetyl and benzoyl derivatives are formed readily.^{593c, 720, 759, 763}

TABLE 1.3
Melting Points of Some Sulfenamides, $RSNR'R''$

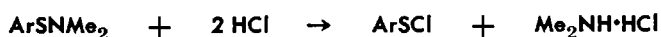
Amine	2-NO ₂ C ₆ H ₄ S	2,4-(NO ₂) ₂ C ₆ H ₃ S	2,4-NO ₂ ClC ₆ H ₃ S
NH ₂	125° ^{77, 759}	—	127° ⁷⁵⁸
MeNH ₂	36° ^{77, 759}	99.5° ⁷⁶	—
EtNH ₂	33° ⁷⁷	66.5° ⁷⁶	—
PrNH ₂	oil ⁷⁷	94.5° ⁷⁶	—
BuNH ₂	28° ⁷⁷	89° ⁷⁶	—
C ₆ H ₁₁ NH ₂	52° ⁷⁷	110° ⁷⁵	—
Me ₂ NH	63° ^{19, 759}	—	—
PhNH ₂	89° ⁷⁷ 94° ⁷⁵⁹	143° ⁷⁶	102° ^{520c} 100° ²⁸¹
<i>o</i> -MeC ₆ H ₄ NH ₂	116° ⁷⁷ 120° ^{520c}	156° ⁷⁶	127° ^{520c} 123° ²⁸⁰
<i>p</i> -MeC ₆ H ₄ NH ₂	136.5° ⁷⁷ 135° ^{520c}	161.5° ⁷⁶	137° ²⁸⁰
<i>p</i> -ClC ₆ H ₄ NH ₂	144° ⁷⁷	164.5° ⁷⁶	172° ²⁸⁰
<i>p</i> -BrC ₆ H ₄ NH ₂	146.5° ⁷⁷	181° ⁷⁶	—
<i>p</i> -MeOC ₆ H ₄ NH ₂	138.5° ⁷⁷	159° ⁷⁶	—
α -C ₁₀ H ₇ NH ₂	131° ⁷⁷ 129° ⁷⁵⁹	189° ⁷⁶	180° ²⁸⁰
β -C ₁₀ H ₇ NH ₂	202.5° ⁷⁷ 188° ⁷⁵⁹	168° ⁷⁶	176° ²⁸⁰

Sulfenimides

(PhS) ₂ NH, m.128° ⁴⁵⁷	(2,4-NO ₂ MeC ₆ H ₃ S) ₂ NH, m.241° ⁷⁶⁸
(<i>o</i> -NO ₂ C ₆ H ₄ S) ₂ NH, m.217° ⁷⁵⁹	(2,4-NO ₂ MeC ₆ H ₃ S) ₂ NMe, m.226° ⁷⁶⁸
(<i>p</i> -NO ₂ C ₆ H ₄ S) ₂ NH, m.155° ⁷⁶⁸	(2,4-NO ₂ ClC ₆ H ₃ S) ₂ NH, m.210° ⁷⁵⁸

With Acids

A sulfenamide is cleaved by hydrogen chloride: ^{76, 77, 758, 759, 762, 763}



In many cases the reaction is practically quantitative and has been used in the preparation of sulfenyl chlorides and bromides.^{456, 457, 520c, 593c, 594} In some cases the cleavage can be effected by concentrated aqueous hydrochloric acid. In case the sulfenyl halide is unstable under the reaction conditions, the disulfide or other decomposition product will be obtained.^{457, 520c, 758}

As has been noted, a hot dilute or weak acid causes the formation of an imide, one molecule of the amine being eliminated from two of the amide.

A sulfenamide, sulfur dioxide, and water give a substituted ammonium alkyl thiosulfate:⁴⁵⁵



Oxidation and Reduction

There are several examples of oxidation in alkaline solution to sulfonamides.^{493, 504}

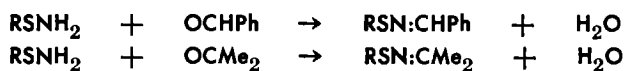


In acid solution, hydrolysis goes along with oxidation and the results are complicated.^{279, 280, 281} The sulfenamide, 2,4-NO₂ClC₆H₃SNHC₆H₄OH-*p* can be oxidised to the quinoneimine, 2,4-NO₂-ClC₆H₃SN:C₆H₄:O.^{278, 279}

It has not been found possible, even under the mildest conditions, to reduce sulfenamides without cleavage of the S-N linkage.^{278, 279}

With Aldehydes and Ketones

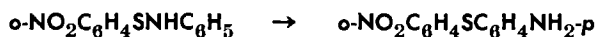
Sulfenamides, in which there are no substituents on the amide nitrogen, react with aldehydes and ketones after the manner of primary amines:^{151, 759, 762, 763}



In the case of α -anthraquinonesulfenamide, this condensation takes place with the adjacent quinone carbonyl.^{260b}

Rearrangement

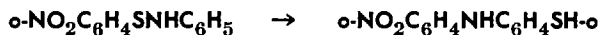
When a sulfenanilide is heated at 150 to 160° for some hours, rearrangement to an amino sulfide takes place to a small extent:^{389, 520c}



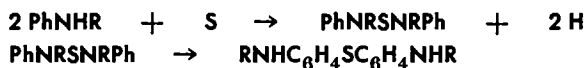
If the heating is done in the presence of an aromatic amine, the reaction goes much further, giving as much as 70% of the amino sulfide. If the *para* position is blocked, the amino group goes to the *ortho*. The amine that is added takes part in the reaction and may replace the one originally in the sulfenanilide. The character of the aromatic amine determines the extent of the displacement. Thus, *o*-chloroaniline will not displace aniline or *o*-toluidine, but is displaced by them. The aromatic amines have been arranged in order as to their power to displace other amines.^{387, 520c}

When certain nitro-substituted benzenesulfenanilides are heated in dilute alcoholic sodium hydroxide, the rearrangement

takes an entirely different course and the product is an *o*-mercapto-diaryl amine: ^{520b, 738}



The reaction of sulfur with aniline, or with N-alkylanilines, probably goes in two stages:



The intermediate, in which the sulfur is bound to the nitrogen, cannot be isolated, but it is known that only those amines which have a labile hydrogen on the nitrogen react in this way. ^{520a}

SULFENIC ESTERS, RS·OR'

Formation

These are isomeric with the sulfoxides, RSO·R', but differ from them in properties as well as in the reactions that are used for their preparations. The sulfenic esters belong to the lowest state of oxidation of the sulfur.

RS·OR'
Sulfenic esters

RSO·OR'
Sulfinic esters

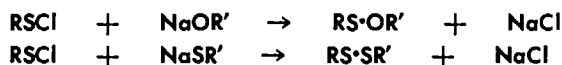
RSO₂·OR'
Sulfonic esters

Corresponding to the sulfonic esters, RSO₂·OR', we have thiosulfonic, RSO₂·SR'. Thiosulfenic esters would be the disulfides.

RS·OR'
Sulfenic esters

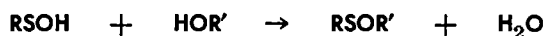
RS·SR'
Thiosulfenic esters

The disulfides are, of course, well known but are not thought of as related to the sulfenic esters. Actually both can be made by similar reactions:

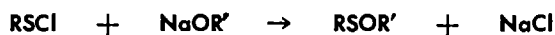


For sulfenic esters, this is the only general method.

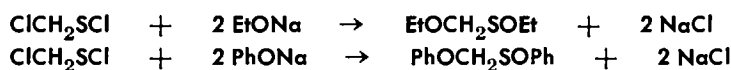
A sulfenic ester can be made by the esterification of a sulfenic acid:



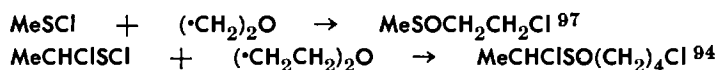
This applies to α -anthraquinonesulfenic acid which is the only sulfenic acid that has been isolated. ^{257, 280b} Other sulfenic esters have to be made from the sulfenyl halides: ⁴⁰⁹



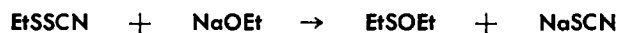
Both chlorine atoms in chloromethanesulfenyl chloride are replaced: ¹⁰¹



Ethylene and tetramethylene oxides are opened up by sulfenyl chlorides:



A sulfenyl thiocyanate may be used: ^{510b}



The sulfenyl selenocyanate reacts with an alcohol rather than with the alcoholate: ^{592a}



2,4-Dinitrobenzeneselenenyl bromide, 2,4-(NO₂)₂C₆H₃SeBr, reacts well with an alcohol in the presence of silver acetate, but not with a sodium alcoholate.¹⁵⁶ The same is true of the unnitrate α -anthraquinoneselenenyl bromide.^{381a}

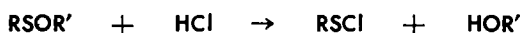
Properties

The melting points of a number of these esters are in Table 2.3.

Reactions

These esters are fairly stable to heat but are readily hydrolyzed, even by moist air.^{453, 758, 759} Comparing the formulae, ArSOR and ArSO·OR, suggests that sulfenic esters might be oxidised to sulfinic. Oxidation of alkyl 2-nitrobenzenesulfenates led to the free sulfinic acids rather than to their esters,⁴⁵³ but oxidation of ethyl ethanesulfenate, EtSOEt, gave the sulfinic ester, EtSO·OEt.^{510b}

Concentrated hydrochloric acid splits a sulfenic ester: ^{756, 758, 759, 762, 763}



Alkaline hydrolysis of a sulfenic ester might be expected to give a sulfenic salt:

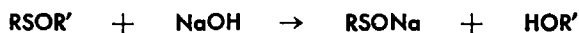


TABLE 2.3
Some Alkyl and Aryl Sulfenic Esters

EtSOEt, b_{50} 38.2–8.5° b_{724} 107.8–8.5° ^{510b}	2,4-(O ₂ N) ₂ C ₆ H ₃ SOR Me, m.125° ⁵⁶¹ 123° ⁴¹⁶
<i>t</i> -BuSOEt, $b_{8.9}$ 64° ^{590b} , ⁵⁹⁵ b_{90} 65° ⁵⁸	Et, m.125° ⁴¹⁶ , ⁵⁶¹
PhSOMe, b_4 88–9° ⁴⁵⁷	Pr, m.76° ⁴¹⁶
Ph ₃ CSOMe, m.124° ⁷²⁰	<i>i</i> -Pr, m.78° ⁴¹⁶
PhOCH ₂ SOR	Bu, m.54° ⁴¹⁶
Ph, m.168° ¹⁰¹	<i>s</i> -Bu, m.72° ⁴¹⁶
<i>o</i> -O ₂ NC ₆ H ₄ SOR	<i>t</i> -Bu, m.119° ⁴¹⁶
Me, m.54° ⁷⁵⁹	Am, m.32° ⁴¹⁶
Et, m.26° ⁷⁵⁹	<i>i</i> -Am, m.57° ⁴¹⁶
Ph, m.72° ⁷⁵⁹	<i>t</i> -Am, m.103° ⁴¹⁶
C ₆ H ₃ Me ₂ -2,4, m.85° ⁴⁵³	Octyl, m.58° ⁴¹⁶
C ₆ H ₃ Me ₂ -3,5, m.74° ⁴⁵³	Lauryl, m.74° ⁴¹⁶
C ₆ H ₂ Me ₃ -2,4,5, m.103° ⁴⁵³	Cyclohex., m.134° ⁴¹⁶
C ₆ H ₂ Me ₂ Cl-3,5,4, m.120° ⁴⁵³	PhCH ₂ , m.143° ⁴¹⁶
C ₆ H ₂ Me ₂ Cl-2,5,4, m.120° ⁴⁵³	<i>l</i> -Methyl, m.100° ⁴¹⁶
C ₆ HMe ₂ Cl ₂ -3,5,2,4, m.127° ⁴⁵³	α -C ₁₀ H ₇ SOR
<i>p</i> -O ₂ NC ₆ H ₄ SOR	Me, m.189° ²⁵⁷
Me, m.49° ⁷⁶²	Et, m.149° ²⁵⁷ , ^{260b}
2,4-O ₂ NMeC ₆ H ₃ SOR	α -C ₁₄ H ₇ O ₂ SeOR
Me, m.71° ⁷⁶³	Me, m.178° ^{381a}
2,4-O ₂ NCIC ₆ H ₃ SOR	Et, m.146° ^{381a}
Me, m.112° ⁷⁵⁶	<i>i</i> -Pr, m.143.5° ^{381a}
Et, m.74° ⁷⁵⁶	Bu, m.84° ^{381a}
Ph, m.75° ⁷⁵⁶	

The products that can be isolated are disulfides and "disulfoxides" which may be supposed to come from sulfenic acids.⁷⁵⁸

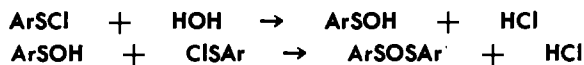
The reaction with a Grignard reagent gives a sulfide:²⁹²



The rearrangement of sulfenic esters resembles that of the sulfenamides. The product is a hydroxy sulfide. A phenol with which the ester is heated may replace the one originally present.^{453, 454b}

SULFENIC ANHYDRIDES, $RS\cdot O\cdot SR$

Sulfenic anhydrides are frequently formed in the hydrolysis of sulfenyl chlorides. They may be supposed to be formed from the sulfenic acid and the unhydrolyzed chloride: ^{756, 758, 759, 762, 763}



Thus, when 2-nitrobenzenesulfenyl chloride is shaken 5 hours with 20 parts of water at room temperature, it is converted into the anhydride. The anhydride is converted by concentrated hydrochloric acid back to the sulfenyl chloride almost quantitatively. This is effected also by phosphorus pentachloride.

The aryl sulfenic anhydrides are solids which melt, or decompose, at relatively high temperatures.

Alkaline hydrolysis might be expected to give a sulfenic salt:

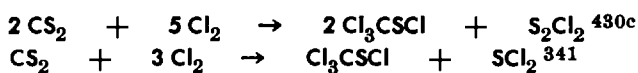


Actually the products are a sulfinate and a disulfide.

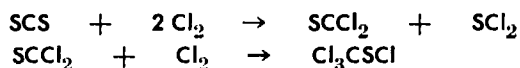
PERCHLORMETHYLMERCAPTAN, Cl_3CSCI *Formation*

It is probable that this compound was present in the mixture of products which Kolbe obtained in 1843 when he added some carbon disulfide to a roomy flask filled with chlorine and let it stand for some days. Better results were obtained by using a chlorine-generating mixture of manganese dioxide and hydrochloric acid.^{436a} This experiment was repeated by Rathke who found it more practical to pass chlorine into carbon disulfide containing a small amount of iodine.^{585b} This is essentially the method that has been used ever since. The yields have been raised from around 15% to 60–5% by attention to details.^{43a, 237, 251, 388a, 390, 404, 618, 621}

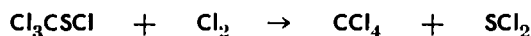
The reaction has been written:



The optimum amount of chlorine is said to be 2.7Cl_2 to 1CS_2 .^{213, 216} It is probable that the reaction goes in two stages: ^{430c}



The desired product can be chlorinated further:



This is favored by the presence of iron.^{178, 341} In fact, this is the accepted method of manufacturing carbon tetrachloride.

Chlorine is passed into carbon disulfide until its volume is doubled,³⁴¹ or until its weight is 3.5 times the original.^{213, 216} Iodine is always used as a catalyst; 0.1% is sufficient. Four things are to be avoided: too much light, too high a temperature, overchlorination, and the presence of iron. None of the desired product can be isolated if the chlorination is carried on at a high temperature or in sunlight. The temperature should be 25°, ^{213, 216} or not above 30°. ⁶²¹ There seems to be no information as to just how much light can be tolerated.

There are many variations in the methods of working up the mixture. Sulfur dichloride may be distilled off. Water, hot or cold, is added to decompose the chlorides of sulfur. The liquid remaining is steam-distilled, once or twice, to get rid of sulfur and other nonvolatile materials. The product is dried and fractionated at reduced pressure. The addition of sulfur trioxide to the reaction mixture is said to raise the yield to 82%.³⁹⁵ A continuous process has been described.⁵⁴⁰ Other improvements have been suggested.^{141, 566}

Some perchlormercaptan is formed in the chlorination of methyl thiocyanate. By the same treatment, ethyl thiocyanate gives the homolog, $\text{CH}_3\text{CCl}_2\text{SCl}$.³⁷⁸ This type of compound has been mentioned under chlorination of dithio esters.

Carbon selenosulfide, suspended in water through which chlorine is bubbled, gives perchlormercaptan. If bromine is substituted for the chlorine, the product is the analog, Br_3CSBr , d. 20/4 3.0240.¹⁰³ Chlorination of carbon diselenide in carbon tetrachloride gives the analogous perchlorselenomercaptan.^{375,5}

Properties

Perchlormethyl mercaptan boils at 147.5–8°, ^{43a} or at 73° at 50 mm. ^{341, 395} It has d 15/4 1.698, ^{43a} d 20/4 1.6996, d 25/4 1.6923.¹⁰³ Other values are: d 11/4 1.71785; n 11/D 1.54835; ¹²⁷ and b_{25} 51°; d 0/4 1.7278, d 20/4 1.6947; n 20/D 1.5395.¹⁹⁷ The surface tension at 20° is 35.02 dynes/cm. from which the mole-

cular parachor is 266.1.¹⁰³ In benzene, the dipole moment is 0.65 and the molar polarization, calculated for infinite dilution, is 43.2. In carbon tetrachloride, these values are 0.56 and 40.8.⁶⁰⁵ The Raman spectrum is similar to those of carbon tetrachloride and of sulfur monochloride which agrees with the structure Cl_3CSCl .²⁰⁹

It is lachrymatory and toxic, but as its odor is stifling, it is more disagreeable than dangerous.³⁴¹ Mice and cats died in 1 or 2 days after inhaling air containing 0.35 mg./liter of it.²⁴³

Reactions

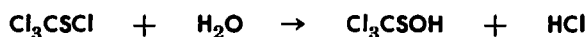
Perchlormethylmercaptan is a sulfenyl chloride. In its chemical properties it resembles other sulfenyl chlorides, but is far less reactive. It can be added to unsaturates.⁵² In contrast to other sulfene chlorides, this addition is sluggish and little is known as to how it takes place. Perchlormercaptan is relatively stable with water, as evidenced by the fact that it can be steam-distilled. With water at 160° or in dilute acid solution, it is decomposed:^{318c}



The simple hydrolysis has been written:⁸²



It seems more probable that it is:



Oxidation by nitric acid gives the sulfone chloride:^{585d, 621}

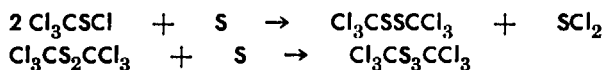


This chloride is obtained directly when moist carbon disulfide is chlorinated.^{436b} The oxidation can be effected in boiling acetic acid. The sulfone chloride melts at 140.5°⁶²¹ and boils at 170°.^{436b} It is formed when perchlormercaptan or trithiane is oxidised by chlorine in cold water.¹⁹⁹ It can be reduced to the sulfinic acid, $\text{Cl}_3\text{CSO}_2\text{H}$.⁴⁷⁶

The sulfone chloride is remarkably stable and unreactive. It can be recrystallized from hot water or alcohol and does not react with ammonia or amines under ordinary conditions.³²⁶ Boiling water decomposes it into carbon dioxide, sulfur dioxide, and hydrochloric acid.⁶³ With water at 160°, the products are

carbon dioxide, hydrochloric acid, and sulfur.^{585b} It is hydrolyzed by potassium hydroxide and is reduced by hydrogen sulfide^{436b} or by potassium sulfite^{585a} to the dichloro-acid, $\text{Cl}_2\text{CHSO}_3\text{H}$.

Perchlormercaptan reacts with sulfur: ^{430c}, ^{585b}, ⁶¹⁸



This is effected by heating the two together at 150 to 160°. Fractionation of the product gives disulfide and trisulfide.^{430c} The disulfide boils at 130° at 10 mm. and the trisulfide melts at 57°, ⁶¹⁸ 57.4°, b. 220°. ^{585b} The trisulfide ^{585b} and the tetrasulfide¹⁷⁸ have been isolated from the residue from the distillation of the crude perchlormercaptan. This residue is probably a mixture of polysulfides in equilibrium with each other and with sulfur.

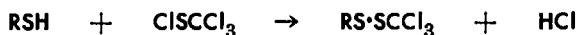
The reaction with potassium sulfite is involved. The product is the salt of mercaptomethanetrisulfonic acid, $\text{HSC}(\text{SO}_3\text{K})_3$.⁵, ^{43a}, ^{43b}, ^{153a}, ^{585b} Perchlormercaptan reacts regularly with potassium cyanide to form the thiocyanate, Cl_3CSCN , m. 2.5°; ⁵⁴¹ ^b₁₆ 55°, ^b₅₀ 79°; ¹⁰⁰ ^d₂₀ 1.585; ¹⁰⁰, ⁵⁴¹ ⁿ 20/D 1.5222.⁵⁴¹ With a Grignard reagent, a trichloromethyl sulfide is formed: ⁶¹⁸



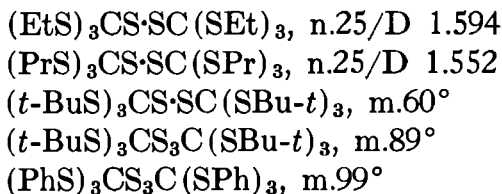
The product of its reaction with a sodium sulfinate is a thiol-sulfonate: ^{50c}, ¹¹⁰, ⁴⁷¹



The product has the following physical constants: ^b₂ 148–50°; ⁿ 25/D 1.601; ^d₂₅ 1.583. The *p*-tolyl compound melts at 65° and the 2,4,6-trimethylphenyl, at 86.5°. ^{50c} With a mercaptan, there is the usual formation of a disulfide: ^{50a}



With a sodium mercaptide the chlorine atoms are replaced by –SR, or –SAr, and the mixed disulfide is replaced by a mixture of the two symmetrical sulfides. A trisulfide may be formed.^{50b}

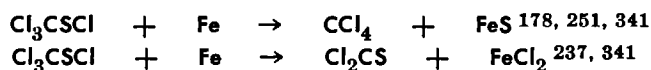


A sodium alcoholate strips off the sulfur as well as the chlorine. The product is an orthocarbonic ester: ^{651, 701}

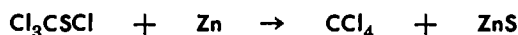


Reduction

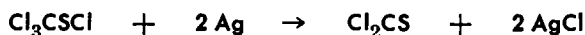
With iron, either sulfur or chlorine is removed:



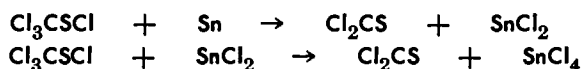
Zinc removes the sulfur: ^{585b}



Silver takes half of the chlorine: ^{585b}



The reduction by tin or by stannous chloride is the most important: ^{38, 153b, 213, 216, 237, 388a, 390, 404}



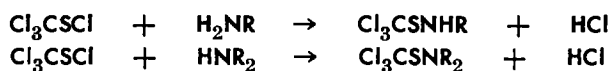
This is the accepted preparation method for thiophosgene. Many, if not most, of those who have made perchlormercaptan have had this use in mind.

Perchlormercaptan is reduced by sodium arsenite to sodium sulfide.^{318c} Zinc may reduce it all the way to methane.³⁴¹ Its reaction with thiosulfate, in the presence of potassium iodide, is much like that of sulfur monochloride.⁵⁶²

Prolonged irradiation of perchlormercaptan gives carbon tetrachloride, thiophosgene, and sulfur chloride.²³⁸

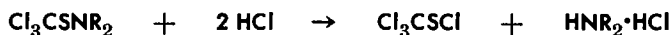
With Amines

Perchlormercaptan reacts with primary ^{153c} and secondary ³⁰ amines:

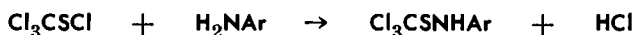


The derivatives of the dialkyl amines are much more stable than those from the primary: $\text{Cl}_3\text{CSNMe}_2$, $b_{15} 74^\circ$; $\text{Cl}_3\text{CSNMe}_2$, $b_{15} 96^\circ$; $i\text{-Bu}_2\text{NSCCl}_3$, $b_{15} 127^\circ$. The reaction is reversed when

hydrogen chloride is passed into a solution of the compound in a hydrocarbon: ³⁰



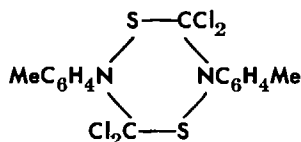
The reaction with aromatic amines is similar: ^{388b, 585b, 585c}



Alcoholic potash abstracts hydrochloric acid to give a cyclic compound: ^{388b, 585c}



According to later investigators, the primary product from *p*-toluidine is $\text{MeC}_6\text{H}_4\text{NHCCl}_2\text{SCI}$. Two molecules of this condense, with the loss of hydrogen chloride, to 2,2,5,5-tetrachloro-1,4-di-*p*-tolyl-1,2,4,5-tetrahydro-3,6-dithiapyrazine, *m.* 142.5° dec.:



In ether solution, this is split by hydrogen chloride to give trichloromethyl mercaptan, Cl_3CSH , *b*₁₅ 125°. This is oxidised by air to the disulfide, $\text{Cl}_3\text{CS} \cdot \text{SCCl}_3$, *m.* 96°. ^{153a} Dyes are formed by the reaction of perchlormercaptan with tertiary aromatic amines. ^{30, 231a}

Perchlormercaptan reacts with an imide or the sodium salt of an imide, putting the $-\text{SCCl}_3$ group for the imide-hydrogen. ^{426, 674c}

Applications

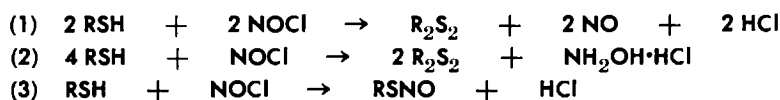
Perchlormercaptan has been suggested as an addition to Diesel fuels. ^{537, 641} Its reaction product with phthalimide is being manufactured on a considerable scale as a pesticide. ^{426, 674c}

Esters of Thionitrous and Thionitric Acids

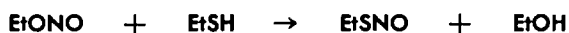


The unstable phenyl thionitrite, PhSNO , is obtained by the reaction of nitrosyl chloride on phenyl mercaptan. ⁶⁰⁵ This reaction takes place with aryl and alkyl mercaptans. ^{590a, 591} Three

different reactions occur between a mercaptan and nitrosyl chloride:

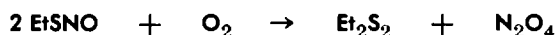


Reactions (1) and (2) are favored, but at -50° , ethyl mercaptan, diluted with a solvent, reacts according to (3) to the extent of about 80% and according to (1), only 10%. It is difficult to separate from the solvent. It is simpler to obtain the ester by the reaction of a mercaptan with ethyl nitrite:



This goes smoothly at -20° . It is remarkable that the mercaptan displaces the alcohol and that the reaction is not reversible as should be expected. Triphenylmethyl thionitrite, Ph_3CSNO , is obtained quantitatively from Ph_3CSH and EtONO . In this, a tertiary mercaptan replaces a primary alcohol.⁴⁵⁹

Ethyl thionitrite, $b_{95} 19-20^\circ$, decomposes slowly at low temperatures, 2% in $4\frac{1}{2}$ hours at 13° , and rapidly at higher temperatures. It is extremely sensitive to atmospheric oxygen:

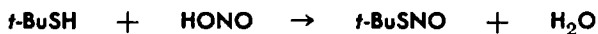


Some ethanesulfonic acid, EtSO_3H , is formed. In the absence of air, ethyl thionitrite decomposes slowly:

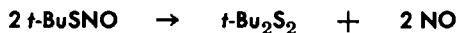


The striking thing about these thionitrites is their intense color. One drop of ethyl or amyl mercaptan added to 55 cc. of ether containing ethyl nitrite gives a distinct color.⁴⁵⁹

Thionitrites from primary and secondary mercaptans are unstable.^{590a} However, nitrosyl chloride reacts smoothly with tertiary butyl mercaptan to give a stable thionitrite, $t\text{-BuSNO}$, m. -54° ; ⁵⁹⁴ $b_{55} 38-9^\circ$, $b_{72} 46-7^\circ$.^{591, 594} This is a red-green liquid. The tertiary amyl compound, $t\text{-AmSNO}$, $b_{44} 38^\circ$, is similar.⁵⁹¹ The mercury mercaptide, $(t\text{-BuS})_2\text{Hg}$, reacts satisfactorily with nitrosyl chloride at a low temperature.^{591, 594} Nitrogen trioxide may be substituted for the nitrosyl chloride.⁵⁹¹ The tertiary butyl is formed when the mercaptan is treated with nitrous acid at 0° or below: ^{668b}



It decomposes in the same way as the ethyl, but only on heating: ^{593a}

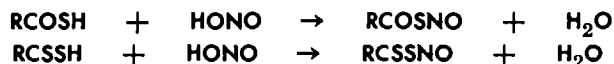


Triphenylmethyl thionitrite, Ph_3CSNO , is stable and can be kept for years, though heated at 100° in a vacuum, it gives off nitric oxide. ⁵⁹¹

Warmed with nitric acid, in acetic acid solution, tertiary butyl thionitrite is oxidised to the thionitrate, $t\text{-BuSNO}_2$, m. -12° ; b_{13} $54-4.5^\circ$. This is a colorless lachrymatory liquid with an exceedingly penetrating odor. ^{593b} The thionitrate can be made directly by passing nitrogen tetroxide into an ether solution of tertiary butyl mercaptan. ²⁸³

Mercaptoacetanilide, though a primary mercaptan, gives a stable thionitrite, $\text{ONSCH}_2\text{CONHPh}$, m. 160° . ⁵⁹⁷

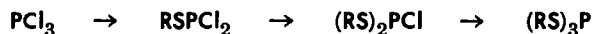
Thio- and dithio-acids react with nitrous acid:



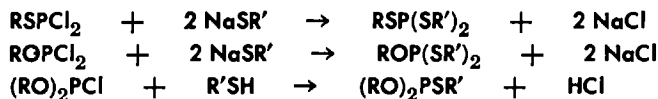
Alkyl thionitrites are useful as additions to Diesel fuels. ^{284, 285, 536, 674a} Various compounds are claimed as stabilizers for thionitrites in Diesel fuels. ¹⁶⁴

Trithiophosphites, $(\text{RS})_3\text{P}$

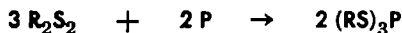
When phosphorous trichloride and a mercaptan are mixed, without a solvent, the halogen atoms are replaced progressively by $-\text{SR}$: ^{430a, 430b}



The dichloride, EtSPCl_2 , boils at $172-5^\circ$ and has the density 1.30 at 12° . ^{511c} If it is desired to obtain the end product, $(\text{RS})_3\text{P}$, exclusively, pyridine, or better dimethylaniline, is added to the mixture. The intermediate products are useful for making mixed esters: ^{23a}

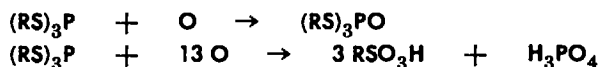


Heating an alkyl disulfide and yellow phosphorus together at 200° gives the trithiophosphite: ⁶⁷⁸



The trialkyl trithiophosphites are colorless oils, insoluble in water but very soluble in the usual organic solvents. They have powerful odors and are readily oxidised by air. All are decomposed by water, alkali, or strong acids.

They are oxidised by 3% hydrogen peroxide to the corresponding trithiophosphates, while stronger oxidising agents break them down into phosphoric acid and sulfonic acids:



Alkyl phosphites are sulfurized by treatment with phosphorus pentasulfide.⁵³⁸

The trialkyl trithiophosphites combine with alkyl halides. With mercuric bromide or iodide or with auric chloride, they give crystalline complexes, many of which have definite melting points.^{23a, 470}

The properties of some straight⁴⁷⁰ and mixed^{23a} thiophosphites are in Table 3.3. More complicated esters are made from ethane-dithiol.²⁵

TABLE 3.3
Some Trialkyl Thiophosphites

Formula	M.p. °C.	B.p. °C.	Pressure mm.	d ⁰ / ₄	d ²⁰ / ₄	n ²⁰ / _D
(EtS) ₃ P	-31	140-3	18	1.1883	1.1585	1.5689
(PrS) ₃ P	-64	164-9	15	1.1277	1.0932	1.5350
(BuS) ₃ P	-100	174-80	15	1.0773	1.0421	1.5305
(EtO) ₃ PSEt	—	75-6	10	—	d ²⁰ / ₄ 1.0211	n ²⁰ / _D 1.4592
(EtS) ₂ POEt	—	108-11	10	—	1.0679	n ¹⁵ / _D 1.5326
(PrO) ₃ PSEt	—	120-4	12	—	d ¹⁵ / ₄ 1.0560	n ¹⁷ / _D 1.5241
(EtS) ₃ POPr	—	128	15	—	1.0487	n ²⁰ / _D 1.5278
(3-C ₄ H ₉ S ₂) ₃ P	—	71.5-73 ^{106, 107}	—	—	—	—

Triamyl and other trialkyl trithiophosphites are claimed as additions to Diesel fuels.¹⁴⁸ The triamyl⁵¹⁶ and "tripinene"⁵⁵⁸ are said to be antioxidants. Straight- or branched-chain trialkyl trithiophosphites are said to improve lubricating oils.²¹² Aryl tri-thiophosphites, in which the radicals may be the same or different,

are recommended as corrosion inhibitors in lubricating oils,^{228, 616b, 644b} or as preventatives of excessive wear.^{201, 228, 559, 616a} The triamyl trithiophosphite is claimed for the same purpose.²²⁹

A product which may be used in oils or as a plasticizer for resins is said to be made by causing a phosphonitrilic chloride to react with a mercaptide.^{469b}

Diethyl thiophosphite, $(\text{EtO})_2\text{PSH}$, does not belong here, as the sulfur is not directly linked to carbon, but it may be mentioned. With chlorine it gives the chloride, $(\text{EtO})_2\text{PSCl}$. With ethyl iodide the diethylphosphonic ester, $\text{EtPS}(\text{OEt})_2$, is formed.^{393c} Polyvalent metal salts of $(\text{EtO})_2\text{PSH}$ are claimed as corrosion inhibitors.⁵³⁰

Thiorarsenious Esters, $(\text{RS})_3\text{As}$

These are by no means well known. They can be prepared by the methods that are used for the trithiophosphites. Arsenic trichloride and a mercaptan are refluxed in benzene solution,⁴³¹ or a sodium mercaptide is added to an alcoholic solution of the trichloride.^{430a, 430b, 432} The triphenyl compound, $(\text{PhS})_3\text{As}$, melts at 95° and the tritolyl at 76° .⁴³² From thiosalicyclic acid, the acid, $\text{As}(\text{SC}_6\text{H}_4\text{CO}_2\text{H})_3$, m. 210° , has been prepared.⁴³¹ From 2-hydroxytrimethylene-diarsenoxide and monothioglycerol, the compound, $(\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{S})_2\text{AsCH}_2\text{CH}(\text{OH})\text{CH}_2\text{As}(\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})_2$, has been obtained.²²⁷

Alkylarsenious mercaptides, $\text{RAs}(\text{SR})_2$, are recommended as seed immunizers.^{371a}

Trithioantimonites, $(\text{RS})_3\text{Sb}$

Our knowledge of these is very meager. They can be prepared from antimony trichloride and mercaptans. The triethyl compound, $(\text{EtS})_3\text{Sb}$, boils at 167 to 170° at 4 mm. and has $d_{0/4}$ 1.6224 and $d_{25/4}$ 1.5873.⁴⁷⁰ A number of compounds of this type have been prepared as oil-soluble therapeutic agents.^{431, 432} The product from ethylene mercaptan is the intermediate chloride, $(\text{CH}_2\text{S})_2\text{SbCl}$, m. 124° .¹⁴² The triphenyl derivative melts at 71° and the tri-*p*-tolyl at 95° . These are made by heating the sodium mercaptide with antimony trichloride in a bomb.⁴³² The thioacetanilide derivative, $\text{Sb}(\text{SC}_6\text{H}_4\text{NHAc})_3$, melts at 165 to 168° .

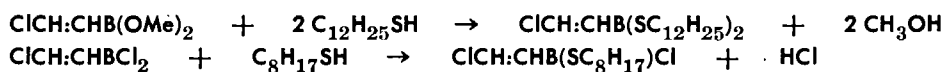
From thiosalicylic acid, two compounds, $\text{Cl}_2\text{SbSC}_6\text{H}_4\text{CO}_2\text{H}$, m. 120° , and $\text{ClSb}(\text{SC}_6\text{H}_4\text{CO}_2\text{H})_2$, m. 86° , have been prepared.⁴³¹

Bismuth Compounds

The bismuth compound, $\text{Bi}(\text{SEt})_3$, is a yellow powder, melting at 200° . It can be considered to be a mercaptide rather than an ester^{430b, 470} and is treated in Chapter 2.

Thioboric Esters

The fact that mercaptans are not esterified by boric acid, while alcohols are, is the basis for a method of separation.⁶⁴⁰ β -Chlorovinylboron esters have been made by transesterification and from the chloride:⁴⁵²



They can be made from boron tribromide and mercaptans.³⁰⁶ Tributyl trithioborate is claimed as a corrosion inhibitor in lubricating oils.^{644a}

Thiophosphoric Esters

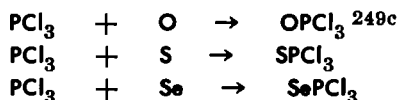
FORMATION

Formulae can be written for a variety of thiophosphoric acids:

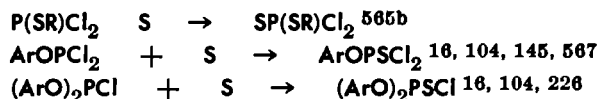


Besides these, there are thiopyrophosphoric and thiometaphosphoric acids. Esters of all of these are known. Esters having two or three different alkyls and ester-chlorides can be prepared. Many of these have been made, but only a fraction of the possibilities has been realized. There has been intense activity in this field as many of these compounds have found commercial applications. On account of the number and variety of the compounds, it is impossible here to give more than a few examples of the great many that have been prepared. Strictly speaking, the esters SP(OR)_3 do not belong here since they are not mercaptan derivatives, but they are included for comparison and because they can be isomerized into mercapto-esters.

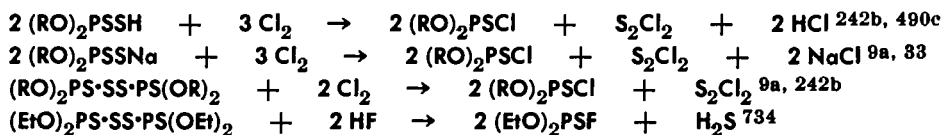
Phosphorus trichloride takes up oxygen, sulfur or selenium:



Sulfur can be added to an ester-chloride:

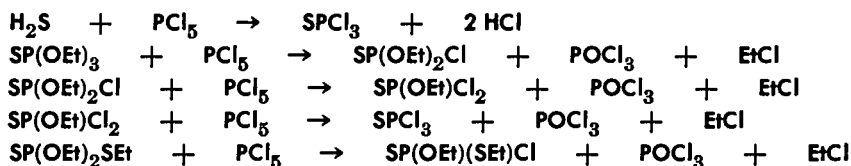


Various derivatives of dithiophosphoric acid can be chlorinated:



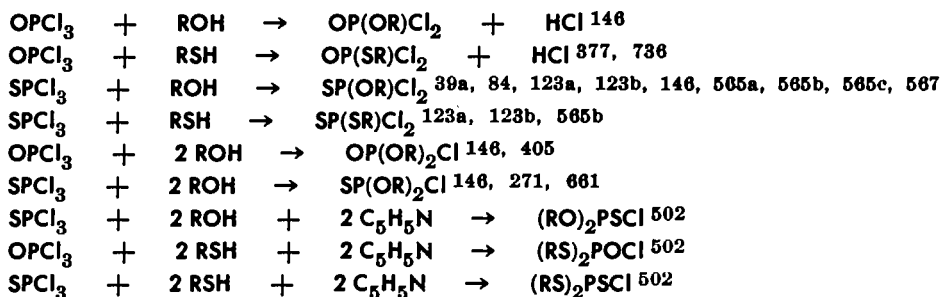
Fluorination of EtOPSCl_2 gives a mixture of EtOPSClF and EtOPSF_2 .⁸⁴

Phosphorus pentachloride reacts with hydrogen sulfide⁵⁶⁷ and with thiophosphate esters: ^{123a, 123b, 440}

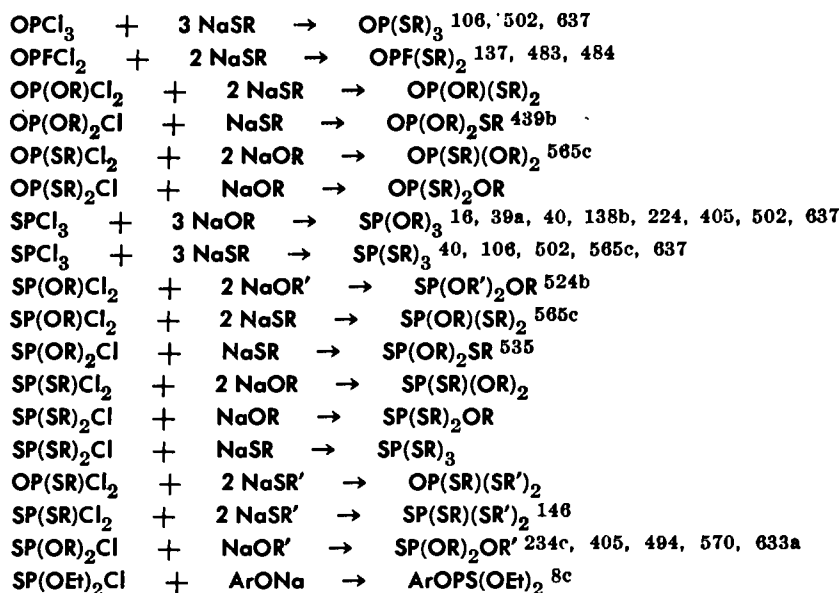


In making an arylthiophosphate, phenol, or a cresol, phosphorus pentachloride and hydrogen sulfide may be put in together.⁶⁴⁵

In the absence of a base, or in the presence of a limited amount of a base, alcohols, phenols, and mercaptans react incompletely with phosphorus oxychloride or sulfochloride:

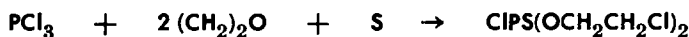


These reactions go to completion in the presence of excess base. By starting with the ester-chlorides all manner of mixed esters can be prepared:

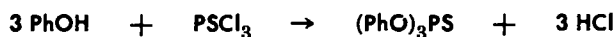


There may be, of course, ester interchange.

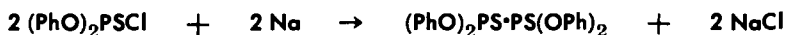
Phosphorus trichloride, sulfur, and ethylene oxide react: ^{439a}



Phosphorus trichloride catalyzes the reaction of phenol with phosphorus sulfochloride:



Refluxing the mixture for 7 hours in its presence causes the evolution of 99.5% of the calculated hydrogen chloride.³⁰⁵ Two molecules of a monochloride can be coupled by the use of sodium:



The product is useful as an extreme-pressure lubricant.²²⁵

Trithio- and tetrathio-phosphates have been made from phosphorus oxychloride and thionophosphorus chlorides and 3-thiophenethiol with the aid of pyridine.¹⁰⁷

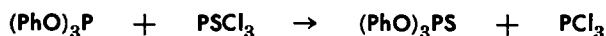
A dialkyl phosphite and a sulfenyl chloride give a monothio-phosphate: ^{233a, 233b}



Trialkyl and triaryl phosphites take up sulfur: ^{14, 15, 16, 25, 26, 29, 104, 470, 524a}

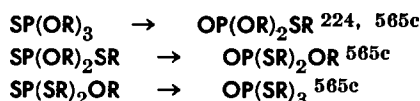


This is true also of dialkyl phosphites, $(RO)_2POH$,^{249c} and of tetraalkyl pyrophosphites.²¹ The sulfur may come from phosphorus sulfochloride: 16, 305



Selenium also is taken up.^{249c} When the ester, $(EtO)_2PSH$, is treated with sodium in benzene and sulfur added, the dithiophosphate ester, $(EtO)_2PSSH$, is formed.^{393c}

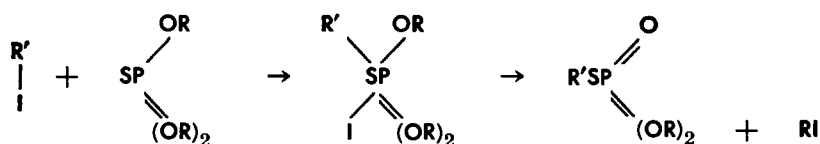
Esters having the $SP(OR) <$ group rearrange into those with $OP(SR) <$:



This takes place when the ester is heated in a sealed tube with an alkyl iodide. If the alkyl iodide has a different radical it appears in the new ester:

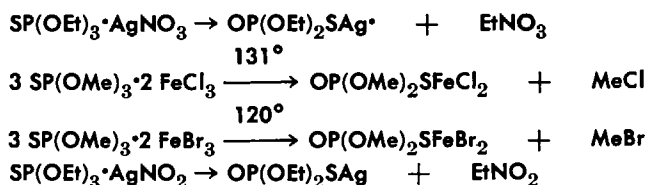


This indicates an intermediate of a sulfonium type:

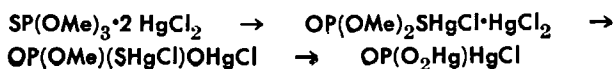


With drastic treatment, the end product is the sulfonium iodide.²²⁴ This isomerization takes place, though to a less extent, when the ester is heated alone, with water, with methanol, or with hydrogen chloride in methanol.²²⁴

The $SP(OR)_3$ esters form complexes with a number of metal salts.^{123b} These decompose on heating: 565b



With mercuric chloride the decomposition of the addition compound takes place in stages: 565b



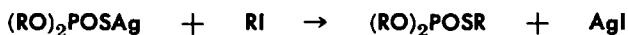
Methyl chloride is given off at each stage. The thallium chloride complex decomposes similarly: ^{565a}



These reactions may involve the formation of a sort of sulfonium complex:



The formation of the triethyl ester, SP(OEt)_3 , from SPCl_3 and sodium ethylate is accompanied by that of two sodium salts: $\text{EtOPSO}_2\text{Na}_2$ and $(\text{EtO})_2\text{PSNa}$, from which other salts can be prepared.^{424b} These should probably be written OP(OEt)(ONa)SNa and $\text{OP(OEt)}_2\text{SNa}$ or as equilibrium mixtures.^{234b} Silver salts, $\text{OP(OR)}_2\text{SAg}$, have been reported.^{224, 565a, 565b, 565c} These are the same silver salts that are obtained by the decomposition of the silver nitrate complexes: $\text{SP(OR)}_3 \cdot \text{AgNO}_3$. They react with alkyl halides: ^{224, 565a}



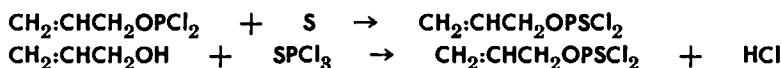
Salts of other metals react similarly.^{24, 232a, 234a, 633b} This gives another route from $(\text{RO})_3\text{PS}$ to $(\text{RO})_2(\text{RS})\text{PO}$.^{565a}

Thiophosphoric esters have been obtained by the addition of thiophosphoric acid to an unsaturate^{10, 129, 186b, 351b, 386, 505} and by the reaction of an olefin sulfide with phosphoric acid.²

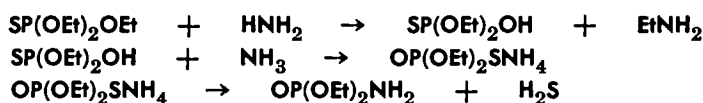
Phosphorus sulfochloride, SPCl_3 , and a number of ester-chlorides and esters made from it, MeOPSCl_2 , EtOPSCl_2 , PrOPSCl_2 , *i*-AmOPSCl₂, $(\text{MeO})_2\text{PSCl}$, $(\text{EtO})_2\text{PSCl}$, $(\text{MeO})_3\text{PS}$ and $(\text{EtO})_3\text{PS}$, are oxyluminescent.¹⁷⁷ The ester, $(\text{MeO})_3\text{PS}$, has the odor of ozone.⁶⁴⁷ The absorption spectrum of the triethyl ester, SP(OEt)_3 , has been compared to those of triethyl phosphate and inorganic phosphates.⁶⁸⁸ The same has been done for the Raman lines of the trimethyl ester.⁶⁴⁷

Ethyl esters containing only oxygen or only sulfur distil at atmospheric pressure without decomposition. Those containing both decompose at about 160°. An alkyl sulfide is one of the products. Ethyl thiophosphites with only one or two sulfur atoms can be steam-distilled.^{123a, 123b}

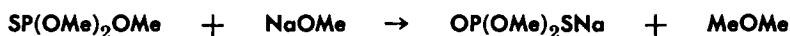
The allyl ester-chloride has been made by the addition of sulfur to the allyloxyphosphorus chloride as well as by the reaction of the alcohol on the sulfochloride: ⁵⁶⁷



The esters SP(OR)_3 are comparable to the sulfates, $\text{O}_2\text{S(OR)}_2$, as alkylating agents. Ammonia is alkylated by the triethyl ester at 120° . The reactions may be: ^{565b}



The trimethyl ester reacts similarly with sodium methylate: ²²⁴

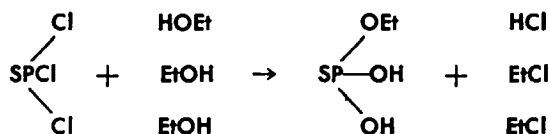


With sodium sulfhydrate it goes further: ²²⁴

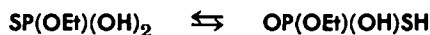


The salt $\text{MeOPSO}_2\text{Na}_2 \cdot 6 \text{H}_2\text{O}$ melts at 49° . ²²⁴

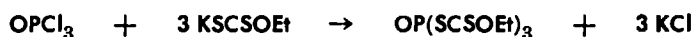
Phosphorus sulfochloride may react with alcohols in another way. ^{138b, 147}



There may be an equilibrium:



Phosphorus oxychloride reacts with a xanthate:



On heating, this decomposes to give an ethyl polysulfide. ⁶⁰⁰

Aryl trithiophosphates, $(\text{ArS})_3\text{PO}$, are claimed as oxidation inhibitors. ⁷⁰⁹ The triphenyl and triamyl esters, $(\text{RS})_3\text{PO}$, are said to be good in extreme-pressure lubricants. ³⁶⁸

The thiol esters, OP(SR)(OR)_2 , are usually prepared by isomerizing the thion esters, SP(OR)_3 . ^{224, 565c} This raises the boiling point, at 20 mm. pressure, by about 20° and increases the density.

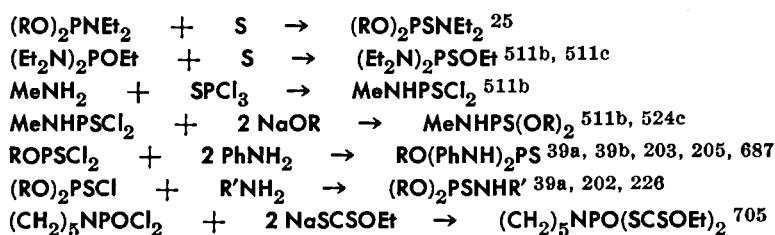
There are acid esters, $\text{SP}(\text{SEt})_2\text{OH}$, $\text{SP}(\text{SEt})(\text{OEt})\text{OH}$ or $\text{OP}(\text{SEt})(\text{OEt})\text{SH}$, $\text{SP}(\text{SEt})_2\text{OH}$ or $\text{OP}(\text{SEt})_2\text{SH}$ and $\text{SP}(\text{SEt})_2\text{SH}$.^{511a, 511c}

The addition product of bromine to phosphorus trisulfide reacts with ethanol to give esters of thiopyrophosphoric acid $\text{P}_2\text{S}_3(\text{OEt})_3\text{Br}$, $\text{P}_2\text{S}_3(\text{OEt})_2(\text{SEt})_2$ and $\text{P}_2\text{S}_3(\text{OEt})_4$. Sulfuric acid converts triethyl thiophosphate into tetraethyl dithiopyrophosphate:^{123b}



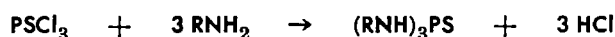
AMID-ESTERS

There are several routes to amid-esters of thiophosphoric acids:



One product of this class is said to be useful in treating yarn;^{186a} others are pesticides, their chief use. Mixed aryl-alkyl ester-amides, $p\text{-NO}_2\text{C}_6\text{H}_4\text{OPS}(\text{NR}_2)\text{OEt}$, have been described.^{203, 204, 205, 525}

Phosphorus sulfochloride reacts with ammonia and with amines:^{41, 138a, 614}



A molecule of amine can be driven out of thiophosphoric triamide:⁵¹²

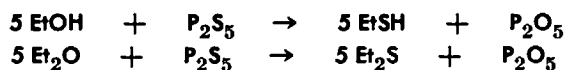


Triamides from morpholine, cyclohexyl amine, piperidine and aniline,^{37, 41, 112} as well as from the simpler amines,^{511b} have been described. Products of this class are said to be useful in high-pressure lubricants.^{469a}

As these thiophosphoric amides and amid-esters do not contain RS- groups, they are not mercaptan derivatives and do not belong in this chapter, but are mentioned for the sake of completeness.

THE REACTION OF PHOSPHOROUS PENTASULFIDE
WITH AN ALCOHOL

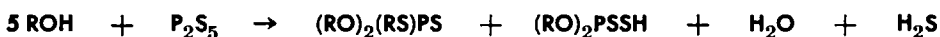
Kekulé, who thought primarily of valence, wrote the famous equations: ⁴⁰⁰



This was in 1854. Since then alcohols and phenols have been treated with phosphorus pentasulfide innumerable times and various useful products have been obtained, but there is still uncertainty as to what the primary reaction is. It has, however, been established that Kekulé's equations are incorrect. Some mercaptan may be obtained but it is certainly not a primary product. A 10% yield of thiophenol from phenol has been reported.⁶⁶

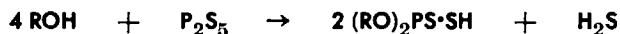
It is well known that, in addition reactions, an alcohol, or phenol, divides into RO- and -H; the oxygen, remaining with the alkyl. The primary products of this reaction must be esters in which the radicals are joined to the phosphorus by oxygen. It is not surprising that, with as complicated a reaction as this is, different investigators have reported divergent results. The conditions for carrying out the reaction and the methods of working up the products influence the results.

According to Carius ^{123a, 123b} and to Kovalevsky ⁴⁴⁰ the reactions with ethanol and with methanol are:



The neutral ester separates as an oil on the addition of water. This has been reinvestigated recently.^{393a} The isoamyl tetrathio-phosphate, (*i*-AmS)₃PS, was reported among the products from isoamyl alcohol.⁴⁴⁰ It is difficult to account for this.

It is now generally agreed that the principal product, that can be isolated, is the dialkyl dithiophosphate, (RO)₂PS·SH.^{121, 242b, 352, 490c, 492a, 502, 565d} The reaction is written:



The yield of this may be as high as 80%.^{490c, 491, 502, 535} A lower sulfide of phosphorus, P₄S₇, does not give the same results.^{393a, 393b}

Cholesterol and phosphorus pentasulfide are reported to give the esters, (C₂₇H₄₅S)₂PO₂H, (C₂₇H₄₅S)(C₂₇H₄₅O)PO₂H and

$(C_{27}H_{45}S)_2P(OH)_3$.⁷²¹ In view of other investigations, the sulfur atoms appear to be misplaced. 2-Nitro-*i*-butanol gives $[Me_2C(NO_2)CH_2O]_2PS\cdot SH$.³⁹⁹

It is known that alkyl phosphates, like the alkyl sulfates, are active alkylating agents. It is possible that some of the products isolated may have resulted from the alkylation of others. The alkylation of $(RO)_2PSSH$ should give $(RO)_2PSSR$ which would hydrolyze to $(RO)_2PSOH$ and HSR , accounting for the mercaptan. Sodium alcoholate may give a sulfide.⁵¹

Treating phenols and alcohols with phosphorus pentasulfide has assumed industrial importance. The crude products are subjected to a minimum of purification, since neither makers nor users are interested in separating and identifying the pure components. One objective has been the making of products which are useful in flotation. Cresylic acid, which has been heated with phosphorus pentasulfide, is called "reconstructed cresylic acid." The chief active agent may be assumed to be a salt of the diester of the dithiophosphoric acid, $(RO)_2PS\cdot SH$.^{8a, 111, 140, 182c, 183a, 324, 363, 379, 608b, 609, 617, 735}

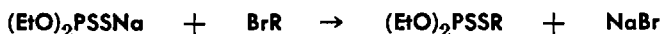
Such products, usually as their heavy metal salts, are recommended as lubricating oil additives, as stabilizers or antioxidants,^{9b, 36, 122, 155a, 252, 265} or as anticorrosion agents.^{122, 287a, 287b, 467, 487, 523, 530, 666a} Some of them are pickling-bath inhibitors.¹⁸¹ Certain of them are useful as extreme-pressure lubricants.^{571, 577, 579} The lead, aluminum, chromium and alkaline earth salts of several are claimed as stabilizers for Diesel oils.⁶¹⁵ Certain thiophosphoric esters are claimed as fuel improvers.⁶¹¹ Aniline may be added to complete the reaction of phosphorus pentasulfide with a hydroxy-compound.⁶⁰ A mixture of an alcohol, or phenol, and a monocarboxylic acid may be subjected to the phosphorus pentasulfide treatment. The products are stabilizers and detergents for lubricating oils.^{8b, 155b} Addition agents for oils have been made from wax-phenols.^{155c, 588, 589a} A cresol may be heated with a mixture of phosphorus and sulfur.⁶⁹⁰ Barium sulfide is used in making barium salts.³⁴

Salts of the acids, $(RO)_2PSSH$, with nitrogen bases, such as guanidine, are said to be plasticizers for neoprene-type materials.¹⁷²

The acids, $(RO)_2PSSH$, in which R is methyl, ethyl, butyl, *s*-butyl, amyl, *i*-amyl, hexyl, heptyl, octyl, allyl, cyclohexyl,

benzyl, phenyl, or one of the tolyls, have been prepared by heating phosphorus pentasulfide with the appropriate alcohol. These give colored precipitates with some heavy metals. They may be used for the determination of molybdenum.¹¹⁶

They may be alkylated by heating their metal salts with alkyl halides or other alkylating agents: ^{61, 234b, 241b, 351a, 359, 535, 613}



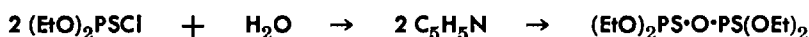
The reaction with phosgene gives a carbonyl tetrathiodiphosphate, $\text{OC}[\text{SPS}(\text{OR})_2]_2$. The ethyl, butyl and tolyl compounds are said to be valuable in the flotation of copper ores.^{241a}

A dialkyl ester of a dithiophosphoric acid, such as $(\text{EtO})_2\text{PSSH}$, is actually a thioacid. As is characteristic of thioacids, these add to unsaturates,⁵³⁵ such as unsaturated ketones,^{351b} maleic esters,^{10, 129, 386, 505} and vinyl ethers.³⁶⁰ Formaldehyde couples them to phenols¹⁵⁴ or to alcohols.³⁶⁰

The dialkyl and diaryl esters, $(\text{RO})_2\text{PSSH}$ and $(\text{ArO})_2\text{PSSH}$, or their salts may be oxidised to the disulfides, $(\text{RO})_2\text{PSSSPS}(\text{OR})_2$ by chlorine or other oxidising agents.^{242b, 249c, 371c, 393b, 485, 491, 515, 545} The products are said to be useful in oils for high-pressure lubricants,⁵⁴⁵ for stabilizers,⁵¹⁵ or for flotation agents.³⁸⁴

A phenol may be heated with phosphorus pentasulfide and the product treated with sulfur chloride to give a polysulfide, $(\text{ArO})_2\text{PS}(\text{S})_n\text{PS}(\text{OAr})_2$.^{275, 515, 585b, 608a, 674b} The products may be vulcanization accelerators^{608a} or additives for lubricating oils.^{275, 515, 589b, 674b} A selenide, $[(\text{RO})_2\text{PSS}]_4\text{Se}$, is claimed as a vulcanization accelerator.⁶⁰⁷ A monosulfide, $(\text{RO})_2\text{PS}\cdot\text{S}\cdot\text{PS}(\text{OR})_2$, is said to be a flotation agent.⁴⁸¹

Dithionopyrophosphates are prepared by the action of water on the thionoester chloride in the presence of pyridine:



An inorganic base can be used, provided some pyridine is present.²³⁵ The toxicity of these esters has been studied.⁷⁰⁷

Phosphorus pentasulfide and ethyl orthoformate give a dithiophosphate, $\text{Et}_3\text{PO}_2\text{S}_2$, of undetermined structure. Ethyl tetra-thiophosphate is obtained with ethyl trithio-orthoformate.^{86, 87}

PHOSPHORUS PENTASULFIDE AND OTHER COMPOUNDS

A mercaptan and phosphorus pentasulfide give a tetrathio-phosphate, $(\text{RS})_3\text{PS}$, and a trithiometaphosphate, RSPS_2 .^{123b, 612b}

The product from benzyl mercaptan is claimed as a flotation agent.^{182c}

Products which are mixtures of unknown composition, but which must certainly contain one or more thiophosphoric esters, are made by heating an olefin with phosphorus pentasulfide. These are worked up in various ways into oil additives. The olefins are usually of molecular weights between 200 and 500.^{11, 174, 401, 402b, 472a, 472b, 472c, 675} Hydrolysis of the product prepared from cyclohexene gives a large amount of cyclohexyl mercaptan indicating that the $C_6H_{11}S-$ group is a part of the thiophosphate ester.³⁶⁷ A compound having the composition, $(C_6H_9PS_2)_2$ has been isolated.²³⁶ A product from oleic acid and a hydroxy-compound, and one from these plus naphthalene, are said to be useful in flotation.^{167b}

Useful products, of unknown constitution, are said to be obtained by heating phosphorus pentasulfide with petroleum hydrocarbons,^{472b, 473, 732} hydrogenated rubber^{402a} or an ester-type wax.⁵²⁷ Naphthalene,^{182b} an alkylated naphthalene,⁴⁸⁶ and benzonitrile^{167a} have been subjected to a similar treatment. Perylene gives a red dye.⁵⁶⁰

Phosphorus pentasulfide reacts with aromatic amines: ^{112, 113, 435}



With a smaller proportion of aniline, the reaction is like that with a phenol, at least as the equation is written: ^{112, 113}



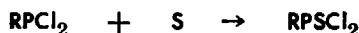
Mixtures of products are obtained from primary and secondary aliphatic amines,⁷⁴³ some of which are claimed as high-pressure lubricants.^{469a}

With camphorimide, phosphorus pentasulfide functions as a sulfur donor, producing dithiocamphorimide.⁴⁹⁶

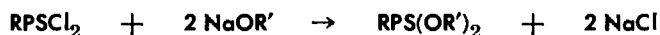
ALKYL AND ARYL PHOSPHINE DERIVATIVES

Some of the following compounds are not mercaptan derivatives but they are mentioned on account of their relations to the phosphorus compounds which have just been considered.

An alkylphosphorus chloride takes up sulfur:

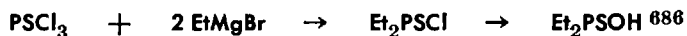


This chloride reacts with a sodium alcoholate:

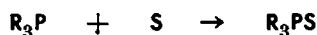


The ethyl, propyl, *i*-butyl and *i*-amyl chlorides have been reported but only one ester.³¹⁴

Phosphorus sulfochloride reacts with the Grignard reagent:

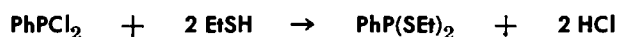


Triethylphosphine and triphenylphosphine take up sulfur: ^{120, 749}

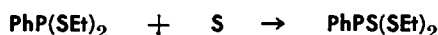


Triethylphosphorus sulfide is described as exceptionally beautiful glistening white crystals.¹²⁰ From diethylphosphine and sulfur, some of this compound is obtained along with the acid Et_2PSSH .³⁵⁵ An isomeric form of the same acid is produced by the reaction of ethylmagnesium bromide on phosphorus pentasulfide.³⁵⁸ The isomerism is explained by assuming different spacial distribution of the groups around the phosphorus atom.^{490a} The reaction of a Grignard reagent with phosphorus pentasulfide is complex, but two of the products finally isolated are R_3PS and R_2PSSH . The methyl, ethyl, *i*-propyl, *i*-butyl, cyclohexyl, and phenyl compounds have been studied.^{490a, 490b, 492b}

In its reactions phenylphosphorus resembles phosphorus closely except that it is quadrivalent instead of pentavalent. The chloride, PhPCl_2 reacts with a mercaptan: ^{22, 492a}



The product combines with sulfur at 150°:



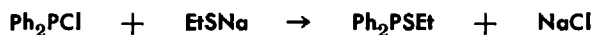
This undergoes partial hydrolysis:



bis-Ethylmercapto phenyl phosphorus reacts with ethyl iodide at 130°: ²²



The diphenyl chloride reacts similarly with a mercaptide:



This is an oil, which, when heated to 100° with ethyl iodide, isomerizes: ²⁰



The benzyl and allyl compounds, $\text{Ph}_2\text{PSCH}_2\text{Ph}$ and $\text{Ph}_2\text{PSCH}_2\text{-CH:CH}_2$, isomerize on standing. ^{23b}

Esters of alkylphosphinic acids take up sulfur just as do those of the phosphorus acids: ²⁷

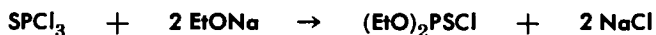


Diethyl *i*-amylthiophosphinate, in lubricating oils, is said to prevent corrosion. ⁶⁹¹ Other esters of this type are claimed as oil additives. ¹⁴³

PARATHION

This is the generally accepted name for the widely used insecticide, O,O-diethyl O-*p*-nitrophenylthiophosphate, $\text{NO}_2\text{C}_6\text{H}_4\text{-O(EtO)}_2\text{PS}$. This was originated by I. G. Farben (their E-605) and the information brought to this country. ^{501, 700} A German preparation was found not identical with an American. ³²¹

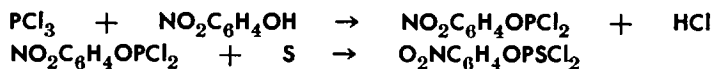
The synthesis, according to the German method with some improvements, has been described in detail. Thiophosphoryl chloride is caused to react with 2 equivalents of sodium ethylate:



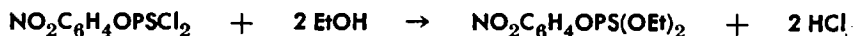
This ester chloride then reacts with sodium *p*-nitrophenoxide: ^{242a}



There are many variations of details in methods of carrying out these reactions. ^{215, 233b, 497, 498, 633c} Other ways of arriving at the same goal have been proposed. The ester, $(\text{EtO})_2\text{PS}\cdot\text{SH}$, from ethanol and phosphorus pentasulfide, is chlorinated to the ester-thiochloride, $(\text{EtO})_2\text{PSCl}$, which is caused to react with sodium *p*-nitrophenate. ^{242b, 708} The order of these steps may be changed. Phosphorus trichloride and *p*-nitrophenol are caused to react and sulfur is added to the product: ¹⁴⁵



The final reaction is with ethanol:

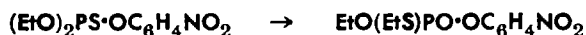


Parathion is formed when tetraethyl thiopyrophosphate is heated with *p*-nitrophenol: ⁷⁴



Several sets of data for the properties of parathion have been given: *b*_{0.5} 157–62°; *n* 25/D 1.5370; ^{242a} *m*.6°; *n* 20/D 1.5384; ^{508b} *m*.5.95 ± 0.05; *d* 25/4 1.2656; *n* 20/D 1.53858. At 25° the surface tension is 39.2 and the viscosity, 15.30.⁷³⁹

Parathion is isomerized by heating at 150° in a sealed tube: ^{508b, 522}



The S-nitrophenyl isomer has been made from diethyl phosphite and *p*-nitrobenzenesulfonyl chloride.^{233a}

For studies of absorption and location in the body of an insect parathion has been synthesized, labeled with S³⁵, ^{382, 474} with P³², ⁵²⁶ and with both of these.³⁴⁰

In the absence of alkali, the hydrolysis of parathion is slow, only 50% in 4 months, but in the presence of lime, it takes place in 8 hours.⁵⁵⁷ The rates of hydrolysis of nitrophenyl esters of phosphoric acid are higher than those of thiophosphoric.⁴⁰⁶

The need for an analytical method ⁷³⁷ has been met in several ways. Parathion may be reduced to the amino compound which is diazotized and coupled to give a dye which is estimated colorimetrically. ^{42, 119, 221, 268, 296, 316, 753} The reduction at a dropping mercury electrode gives a characteristic curve which may be matched by the unknown with an error of ± 1%.⁸⁵ In a cooperative study, a potentiometric method was found to be satisfactory.^{288, 450} After alkaline hydrolysis, the *p*-nitrophenol may be determined.^{375, 606} It may be separated from its isomers by partition chromatography.^{272, 508b} Mosquito larvae may be used in a bioassay.⁵³⁴

The amounts and permanence of residues left on fruits and vegetables have been investigated.^{59, 125, 295, 315, 332, 722, 731}

The attractiveness of this compound as an insecticide has led to extensive studies of possible dangers to man ^{463, 465, 697, 723} and of the physiological effects on animals ^{191, 338, 462, 602, 717} and fish.⁴⁶⁸ Naturally the effects on plants have also been considered.^{166, 298, 301, 575, 581, 639, 652, 653, 719}

There have been many reviews and discussions about para-

thion, its usefulness and applications.^{130, 168, 322, 335, 336, 394, 427, 466a, 499, 563a, 586, 664a, 693, 719, 725, 727} There are many reports and recommendations as to its use in greenhouses.^{79, 184, 334, 353, 503, 656, 658, 659}

Several attempts have been made to determine the mechanism of its action on insects.^{65, 208, 507, 508a}

Unfortunately it is toxic to bees,^{219, 320, 642} as well as to objectionable insects.

It has been tested extensively on a variety of insect pests. Various kinds of aphids^{13, 135, 165, 189, 210, 270a, 282, 337, 366, 392, 443b, 475, 692, 694c, 713, 728b, 740} and mites^{362a, 366, 374, 383b, 392, 421, 514, 521, 531b, 532, 643, 699, 727, 742} have received much attention. Tests have been run on several kinds of moths,^{150, 152, 207, 345, 357, 521, 532} citrus pests,^{230, 546a, 568, 698, 744} curculios,^{80b, 136, 161c, 206, 362b, 603b, 664a, 664b, 728a} gladiolus thrip,^{654, 655} corn^{18, 582, 693} and squash¹²⁸ borers, wire worms,^{188, 449} grasshoppers,^{91, 117, 269, 270c, 312, 313, 554, 598} leaf rollers,^{299, 307, 309, 328, 419, 420, 603a, 694a} army worms,^{356, 693, 702} fruit flies,^{161b, 253, 256, 392} cochineal,^{563b} sheep tick,²⁹⁷ mealy bugs,^{529, 546b, 699} Japanese^{3, 635} and other beetles,^{88, 158, 179, 319, 385, 699, 741a} spittle bugs,^{726, 741b} roaches,^{308, 421} psylla,^{124, 323, 542} boll weevil,^{239, 270d, 475, 583, 619} mosquitoes,^{294, 710} flies,^{220, 286, 354} caterpillars,^{19, 587, 718} corn worms,^{12, 118, 264, 311, 443a, 729} bag worms,⁵⁶⁹ peach borer,^{80a, 521} leaf nematode,¹⁸⁷ migratory locust,^{466b} harlequin bug,^{270b} olive scale,⁸⁷⁰ leaf tier,^{513, 576} saw fly,⁸³ and many other pests.^{17, 105, 159, 161a, 169, 330, 383a, 531a, 601, 610, 694b} At 1 part to 5000 of soil, it is effective against termites for 2 years.³⁴⁷

Other, more or less analogous, thiophosphates have been considered. Two methyl, two propyl, two isopropyl, and an ethyl and a butyl group have been substituted for the two ethyls of parathion and various substituted phenyls for the *p*-nitro.^{508a} *p*-Nitrobenzyl¹⁶² and coumaryl⁶³⁴ groups have been tried in place of the *p*-nitrophenyl. Two or three *p*-nitrophenyl groups are less effective than one. $\text{MeOPS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, $\text{EtOPS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, and $\text{PS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_3$ have negligible activity.⁴⁰⁵ The phenylphosphonates, $\text{PhPS}(\text{OMe})\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$ and $\text{PhPS}(\text{OEt})\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$ are effective.^{214, 380} Aryl ester thiophosphoric amides, $\text{ArOPS}(\text{NR}_2)_2$, have been claimed.²⁰⁰ Tetraethyl dithionopyrophosphate has received the most attention.^{56, 273, 657} It is reported to be superior to parathion.⁵⁶ A dimethyl dithiophosphate¹⁷⁶ and ethyl *p*-nitrobenzenephosphonate have been tested.⁷²⁶

PHYSICAL PROPERTIES OF THIOPHOSPHORIC DERIVATIVES

The properties of some thiophosphoric chlorides and esters are given in the following. The chief purpose is to show the great gaps in our knowledge and the incompleteness of the information about the compounds that have been described. The remarks that were made about "boiling points" in the introduction of the property list in Chapter 1, apply here with equal force. This list, which is far from being complete, does give some information about quite a number of compounds and tells who made them.

The infrared spectra of thirty-four thiophosphates and related compounds have been studied. The $P \leftrightarrow O$ bond absorbs strongly in the region of 1250 to 1300 cm^{-1} . The absorption by the $P \leftrightarrow S$ bond is weak and poorly characterized.³⁰⁴

Dipole moments of a number of esters, $(RO)_3PS$, have been determined.²⁸ $(RO)_3PO$ and $(RO)_3PS$ have similar structures. The three alkoxy chains are parallel.²⁹

Ester-Halides

- MeOPSCl_2 , b_{40} 70°; d 0/4 1.4946.^{565a, 565c}
 EtOPSCl_2 , m . -78.4°; ⁸⁴ b_{20} 68°; d 0/4 1.3966; ^{565a, 565c} b_{20} 52.0°; d 0/4 1.4395.⁸⁴
 $\text{ClCH}_2\text{CH}_2\text{OPSCl}_2$, b_{14} 104-8°; d_{20} 1.4671; n 20/D 1.5362.²⁷¹
 EtOPSClF , b_{20} 26.2°; m . -178°; d 0/4 1.3828.⁸⁴
 EtOPSF_2 , b_{760} 78.4°; m . -124°; d 0/4 1.3019.⁸⁴
 PrOPSCl_2 , b_{20} 80°, ^{565c} b_{20} 84°; ^{565a} d 0/4 1.3341.^{565a, 565c}
 BuOPSCl_2 , b_{10} 81-2°.⁵⁰²
 $i\text{-BuOPSCl}_2$, b_{20} 91°, ^{565a} b_{20} 88°; ^{565c} d 0/4 1.2721.^{565a}
 $i\text{-AmOPSCl}_2$, b_{15} 108-9°; d 0/4 1.2370, d 17/0 1.2188.¹⁷⁷
 $\text{EtOCH}_2\text{CH}_2\text{OPSCl}_2$, b_{23} 108-14°; d_{20} 1.294; n 20/D 1.4910.²⁷¹
 $\text{CH}_2\text{:CHCH}_2\text{OPSCl}_2$, b_{25} 74°.⁵⁶⁷
 EtSPSCl_2 , b_{10} 90°, ^{565c} 92°; d 0/4 1.4450.^{565b, 565c}
 PhOPSCl_2 , b_{16} 132°, ^{39a} b_{26} 150°, ³⁰⁵ b_{11} 119-20°; d 20/4 1.4059.¹⁶
 $m\text{-MeC}_6\text{H}_4\text{OPSCl}_2$, b_{12} 138°.¹⁰⁴
 $(\text{MeO})_2\text{PSCl}$, b_1 40°, ^{9a} b_4 60-3°, ³³ b_{20} 70-2°; n 25/D 1.4795; ^{242b} b_{16} 66°; d 0/4 1.3414, d 17/4 1.3217.¹⁷⁷
 $(\text{EtO})_2\text{PSCl}$, b_{20} 94-6°, ^{242b} b_{25} 96-9°, ⁵⁰² b_{12} 81-2°, ^{393c} $b_{11.5}$ 81.5-3°, ³³ b_8 75°, ^{490c} b_2 60-3°, ⁴⁹¹ b_1 49-50°; ^{9a, 339} d_{20} 1.1918; n 20/D 1.4711, ^{393c} n 25/D 1.4685.^{242b}
 $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{PSCl}$, b_{17} 130°; d_{20} 1.5135; n 20/D 1.5641.²⁷¹

- $(\text{EtO})_2\text{PSF}$, b_{12} 55.6–5.8.⁷³⁴
 $(\text{PrO})_2\text{PSCl}$, b_1 70–5°; n 25/D 1.4672.^{242b}
 $(i\text{-PrO})_2\text{PSCl}$, b_1 56–9°,^{242b} $b_{0.5}$ 55°,^{9a} b_{14} 91°;³³ n 25/D 1.4601.^{242b}
 $(\text{BuO})_2\text{PSCl}$, $b_{0.7}$ 95–8°,^{242b} b_2 95–8°,⁵⁰² b_1 75°;^{9a} n 25/D 1.4670.^{242b}
 $(t\text{-BuO})_2\text{PSCl}$, $b_{0.5}$ 76–82°; n 25/D 1.4624.^{242b}
 $(\text{PhO})_2\text{PSCl}$, m .68°,²²⁶ 67°,^{39a} 64°,^{16, 305} 71°;^{9a} b_{11} 194°,¹⁶ b_1 180–3°.³⁰⁵
 $(p\text{-MeC}_6\text{H}_4\text{O})_2\text{PSCl}$, m .53°.^{39a}
 $(m\text{-MeC}_6\text{H}_4\text{O})_2\text{PSCl}$, m .34°; b_{11} 218°.¹⁰⁴
 $(p\text{-ClC}_6\text{H}_4\text{O})_2\text{PSCl}$, m .92°.^{39a}
 $(\text{EtS})_2\text{POCl}$, b_{22} 145–50°.⁵⁰²
 $(\text{EtS})_2\text{POF}$, b_{15} 104–7°.^{137, 483}
 $(\text{EtS})_2\text{PSCl}$, b_2 110–3°.⁵⁰²

Esters

- $(\text{MeO})_3\text{PS}$, b_{20} 82°,^{565a, 565c, 647} b_{12} 78°,^{565a, 565c} 80°;^{224, 647} d 0/4 1.2190,^{565a, 565c} d_{15} 1.2053, $d_{10.5}$ 1.2112; n 10.5/D 1.45830;²²⁴ +2 HgCl_2 , m .102°; + AuCl_3 , m .110°; +2/3 FeCl_3 , m .125°; +2/3 FeBr_3 , m .99°.^{565b}
 $(\text{EtO})_3\text{PS}$, b_{12} 95.5°,⁶⁸⁸ 94–5°,²⁸ b_{16} 100°,^{565a} b_{20} 106°,^{502, 565a} 118°;²⁴ d 0/4 1.0942,^{565c} d 20/4 1.1132,⁶⁸⁸ 1.0756; n 20/D 1.4488,²⁸ n 22/D 1.4520;²⁴ surface tension 29.65 at 20°; parachor 431.2;²⁹ + HgI_2 , m .88°; ^{565a, 565c} +2/3 PtCl_4 , m .103°.^{565b}
 $(\text{PrO})_3\text{PS}$, b_{10} 123.5–4.5°,^{28, 29} b_{20} 133–4°; d 0/4 1.0407,^{565c} d 20/4 1.0177; n 20/D 1.4502;^{28, 29} surface tension 28.47 at 20°; parachor 545.4.²⁹
 $(\text{BuO})_3\text{PS}$, b_{11} 158–9°; d 20/4 0.9871; n 20/D 1.4515;^{28, 29} surface tension 28.36 at 20°; parachor 660.2°.²⁹
 $(i\text{-BuO})_3\text{PS}$, b_{20} 155°; d 0/4 0.9905.^{565c}
 $(i\text{-AmO})_3\text{PS}$, d_{12} 0.849.^{138b}
 $(\text{HexO})_3\text{PS}$, $b_{2.5}$ 188–8.5°;^{28, 29} d 20/4 0.9501,²⁹ 0.9483; n 20/D 1.4552,²⁸ 1.4568; surface tension 28.68 at 20°; parachor 892.6.²⁹
 $(\text{OctO})_3\text{PS}$, $b_{0.5}$ 224–6°; d 20/4 0.9293; n 20/D 1.4592;^{28, 29} surface tension 29.11 at 20°; parachor 1126.4.²⁹
 $(\text{ClCH}_2\text{CH}_2\text{O})_3\text{PS}$, b_9 142–50°; d 20/4 1.4778; n 20/D 1.5650.²⁷¹
 $(\text{PhO})_3\text{PS}$, m .53°,^{39a} 50°,¹⁶ 49°;⁶³⁷ b_1 232°,³⁰⁵ b_{11} 245°; d 20/4 1.23411.¹⁶
 $(o\text{-MeC}_6\text{H}_4\text{O})_3\text{PS}$, m .45°; b_1 260–5°.³⁴⁴

- $(m\text{-MeC}_6\text{H}_4\text{O})_3\text{PS}$, $m.41^\circ$; b_2 $270-2^\circ$.¹⁰⁴
 $(p\text{-ClC}_6\text{H}_4\text{O})_3\text{PS}$, $m.114^\circ$.^{39a}
 $(\text{EtO})_2\text{PS}\cdot\text{OPh}$, b_{10} 162° .⁵⁷⁰
 $(\text{MeO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $m.38^\circ$,^{242b} 37° ; ^{508b} n 25/D 1.5622.^{8c}
 $(\text{EtO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}o$, n 25/D 1.4882.^{8c}
 $(\text{EtO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $m.6^\circ$; ^{508b} b_2 196° ,⁵⁷⁰ $b_{0.6}$ $157-62^\circ$; ^{242a} d 1.26; ³⁸² n 20/D 1.5384, ^{508b} n 25/D 1.5367, ^{242b} 1.5380, ³⁸² 1.5370.^{8c}, ^{242a}
 $(\text{PrO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $b_{0.5}$ 164° ; n 25/D 1.5259.^{242b}
 $(i\text{-PrO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $m.57^\circ$,^{242b}, ^{508b} 55° .^{8c}
 $(\text{BuO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, n 25/D 1.5195,^{242b} 1.5232.^{8c}
 $(i\text{-BuO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $b_{0.4}$ $167-75^\circ$; n 25/D 1.5155.^{242b}
 $(\text{BuCHEtCH}_2\text{O})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, n 25/D 1.5052.^{8c}
 $(\text{DecO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, n 25/D 1.4940.^{8c}
 $(\text{PhO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, $m.65^\circ$.^{8c}, ^{242b}
 $(\text{ClCH}_2\text{CH}_2\text{O})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{NO}_2\text{-}p$, n 20/D 1.5780.²⁷¹
 $\text{MeOPS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, $m.96^\circ$.⁴⁰⁵
 $\text{EtOPS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, $m.126^\circ$.⁴⁰⁵
 $\text{ClCH}_2\text{CH}_2\text{O}\cdot\text{PS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, $m.96^\circ$.²⁷¹
 $\text{EtOCH}_2\text{CH}_2\text{O}\cdot\text{PS}(\text{OC}_6\text{H}_4\text{NO}_2\text{-}p)_2$, $m.76^\circ$.²⁷¹
 $(p\text{-NO}_2\text{C}_6\text{H}_4\text{O})_3\text{PS}$, $m.174^\circ$.⁴⁰⁵
 $(\text{MeO})_2\text{PS}\cdot\text{OCH}_2\text{CH}_2\text{SMe}$, b_2 115° .^{234c}
 $(\text{EtO})_2\text{PS}\cdot\text{OCH}_2\text{CH}_2\text{SMe}$, b_1 $131-2^\circ$.^{234c}
 $(\text{EtO})_2\text{PS}\cdot\text{OCH}_2\text{CH}_2\text{SEt}$, b_1 134° .^{234c}
 $(\text{EtO})_2\text{PS}\cdot\text{OCH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{Me-}p$, b_1 185° .^{234c}
 $(\text{EtO})_2\text{PS}\cdot\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SEt}$, $b_{2.5}$ 168° .^{234c}
 $(\text{MeO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OMe})_2\text{-}m$, $b_{0.6}$ $120-5^\circ$; d_{20} 1.2890; n 20/D 1.5310.⁴⁹⁴
 $(\text{MeO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OMe})_2\text{-}p$, $b_{0.04}$ 105° ; d_{20} 1.2428; n 20/D 1.5230.⁴⁹⁴
 $(\text{EtO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OEt})_2\text{-}m$, $b_{0.15}$ 130° ; d_{20} 1.1991; n 20/D 1.5113.⁴⁹⁴
 $(\text{EtO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OEt})_2\text{-}p$, $b_{0.2}$ 134° ; d_{20} 1.2496; n 20/D 1.5158.⁴⁹⁴
 $(i\text{-PrO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OPr-}i)_2\text{-}m$, d_{20} 1.1352; n 20/D 1.5103.⁴⁹⁴
 $(i\text{-PrO})_2\text{PS}\cdot\text{OC}_6\text{H}_4\text{O}\cdot\text{PS}(\text{OPr-}i)_2\text{-}p$, d_{20} 1.1720; n 20/D 1.5193.⁴⁹⁴
 $\text{MeS}(\text{MeO})_2\text{PO}$, b_{20} 107° ; ^{565c} d 0/4 1.2683, ^{565a}, ^{565c} d_{10} 1.2562; n 10/D 1.46864.²²⁴
 $\text{MeS}(\text{EtO})_2\text{PO}$, b_{14} $112-3^\circ$.^{633b}

- EtS(EtO)₂PO, *b*₂₀ 122°, ^{565c} *b*₂ 98°, ^{633b} *b*₁₆ 120°; ^{565a} *d* 0/4 1.1243. ^{565c}
- PrS(EtO)₂PO, *b*₁ 130.5°. ^{633b}
- PrS(PrO)₂PO, *b*₂₀ 156°; *d* 0/4 1.0532. ^{565c}
- i*-BuS(EtO)₂PO, *b*_{0.5} 105°, ^{633b} *b*₂₀ 138°; *d* 0/4 1.0897. ^{565c}
- i*-BuO(*i*-BuS)₂PO, *b*₂₀ 170°; *d* 0/4 1.0099. ^{565c}
- HexS(EtO)₂PO, *b*₁ 125–30°. ^{633b}
- C₁₂H₂₅S(EtO)₂PO, *b*_{0.5} 185–9°. ^{633b}
- PhCH₂S(EtO)₂PO, *b*₂ 165–70°. ^{633b}
- EtSCH₂S(EtO)₂PO, *b*_{1.5} 129–30°. ^{633b}
- p*-MeC₆H₄SCH₂S(EtO)₂PO, *b*_{0.5} 178°. ^{633b}
- p*-EtC₆H₄SCH₂S(EtO)₂PO, *b*₁ 136°. ^{633b}
- MeSCH₂CH₂S(EtO)₂PO, *b*₂ 134–8°. ^{633b}
- EtSCH₂CH₂S(EtO)₂PO, *b*₁ 137–41°. ^{633b}
- (EtO)₂PO·SCH₂CH₂S·PO(EtO)₂, *b*_{0.5} 190°. ^{633b}
- MeS(MeO)₂PS, *b*₈ 86°, ⁵³⁵ 86–7°, ^{393a} *b*₁₄ 103°, ¹⁷⁷ *b*_{16.5} 101–1.5°; ^{393a} *d* 0/4 1.2587, *d* 17/4 1.2427, ¹⁷⁷ *d* 20/20 1.2443, ⁵³⁵ *d*₂₀ 1.2415; *n* 20/D 1.5292, ^{393a} 1.5285. ⁵³⁵
- EtS(EtO)₂PS, *b*₁ 74–7°, ⁵³⁵ *b*₁₀ 115–15.5°, ^{393a} *b*₂₀ 128°, ^{565c} *b*₂₃ 128–9°; ⁵³⁵ *d* 0/4 1.1336, ^{565c} *d* 20/20 1.1138, ⁵³⁵ *d*₂₀ 1.1156; *n* 20/D 1.5013, ^{393a} 1.5033; ⁵³⁵ + 2 HgI₂, *m*. 86°. ^{565c}
- PrS(PrO)₂PS, *b*₁₁ 115–6°; *d*₂₀ 1.0561; *n* 20/D 1.4955. ^{393a}
- i*-PrS(EtO)₂PS, *b*₁ 73–7°; *d* 20/20 1.0834; *n* 20/D 1.4993. ⁵³⁵
- i*-PrS(*i*-PrO)₂PS, *b*₃ 91–2°; *d*₂₀ 1.0351; *n* 20/D 1.4843. ^{393a}
- BuS(BuO)₂PS, *b*₄ 148–9°; *d*₂₀ 1.0159; *n* 20/D 1.4859. ^{393a}
- OctS(EtO)₂PS, *b*_{0.02} 75–6°, *b*_{0.03} 80°; *d* 20/20 1.0155; *n* 20/D 1.4930. ⁵³⁵
- C₆H₁₃CHMeS(EtO)₂PS, *b*_{0.02} 74–6°; *d* 20/20 1.0179; *n* 20/D 1.4917. ⁵³⁵
- C₆H₁₃CHMeS(PrO)₂PS, *b*_{0.03} 80°; *d* 20/20 0.9970; *n* 20/D 1.4893. ⁵³⁵
- C₆H₁₃CHMeS(BuO)₂PS, *b*_{0.03} 98–9°; *d* 20/20 0.9830; *n* 20/D 1.4870. ⁵³⁵
- c*-HexS(EtO)₂PS, *b*_{0.02} 62°; *d* 20/20 1.0098; *n* 20/D 1.5203. ⁵³⁵
- c*-HexS(PrO)₂PS, *b*_{0.06} 82–3°; *d* 20/20 1.0751; *n* 20/D 1.5135. ⁵³⁵
- c*-HexS(BuO)₂PS, *b*_{0.13} 101–3°; *d* 20/20 1.0475; *n* 20/D 1.5073. ⁵³⁵
- PhCHMeS(EtO)₂PS, *b*_{0.02} 85°; *d* 20/20 1.1401; *n* 20/D 1.5540. ⁵³⁵
- PhCHMeS(PrO)₂PS, *b*_{0.03} 99.5–101°; *d* 20/20 1.1022; *n* 20/D 1.5428. ⁵³⁵

PhCHMeS(BuO)₂PS, *b*_{0.16} 119–21°; *d* 20/20 1.0712; *n* 20/D 1.5315.⁵³⁵

PhCH₂CH₂S(EtO)₂PS, *b*_{0.02} 85–6°; *d* 20/20 1.1395; *n* 20/D 1.5543.⁵³⁵

MeSCH₂CH₂S(EtO)₂PS, *b*₂ 134–8°.^{234c}

EtSCH₂CH₂S(EtO)₂PS, *b*₁ 137–41°.^{234c}

MeCOCH₂CH₂S(EtO)₂PS, *n* 25/D 1.5074.^{351b}

MeCOCH₂CHMeS(EtO)₂PS, *n* 25/D 1.5087.^{351b}

MeCOCH₂CHMeS(*i*-PrO)₂PS, *n* 25/D 1.4998.^{351b}

MeCOCH₂CHMeS(C₁₄H₂₉O)₂PS, *n* 25/D 1.4805.^{351b}

MeCOCH₂CHMeS(PhO)₂PS, *n* 25/D 1.5878.^{351b}

MeO₂CCH₂CH₂S(EtO)₂PS, *b*_{0.01} 65–6°, *b*_{0.025} 77–8°; *d* 20/20 1.1859; *n* 20/D 1.5026.⁵³⁵

MeO₂CCH₂CH₂S(PrO)₂PS, *b*_{0.04} 85–6°; *d* 20/20 1.1241; *n* 20/D 1.4984.⁵³⁵

MeO₂CCH₂CH₂S(BuO)₂PS, *b*_{0.03} 96–7°; *d* 20/20 1.1375; *n* 20/D 1.4942.⁵³⁵

(EtS)₂(EtO)PO, *b*₂₀ 148°; *d* 0/4 1.1619.^{565c}

(EtS)₃PO, *b*₂ 128–32°,⁵⁰² *b*₁₈ 175°,¹³⁷ *b*₂₀ 174–5°; *d* 0/4 1.1966.^{565c}

(EtS)₂(EtO)PS, *b*₂₀ 155°; *d* 0/4 1.1714; + 2 HgI₂, *m*.112°; + 2 HgCl₂, *m*.81°.^{565b, 565c}

(PhS)₃PO, *m*.72°.⁶³⁷

(EtS)₃PS, *b*₂₀ 182°,^{565c} *b*₂ 132–8°,⁵⁰² 118–9°,⁸⁷ *b*_{0.8} 97–100°;⁸⁶ *d* 0/4 1.2227;^{565c} *n* 20/D 1.6201;⁸⁶ + HgCl₂, *m*.84°.^{565b, 565c}

(PhS)₃PS, *m*.86°.⁶³⁷

(PhCH₂S)₃PS, *m*.–13°.^{612b}

Amides

MeNHPSCl₂, *b*₃₃ 115°.^{511c}

EtNHPSCl₂, *b*.216°, *b*₂₀ 115°.^{511c}

PrNHPSCl₂, *b*₁₇ 121°.^{511c}

i-BuNHPSCl₂, *b*.251°, *b*₁₅ 123°.^{511c}

i-AmNHPSCl₂, *b*₁₆ 140°.^{511c}

Et₂NPSCl₂, *b*₁₄ 107°; *d*₁₅ 1.105.^{511c}

Pr₂NPSCl₂, *b*.242°, *b*₁₅ 133°; *d*₁₅ 1.077.^{511c}

i-Bu₂NPSCl₂, *m*.36°; *b*₁₀ 150°.^{511c}

i-Am₂NPSCl₂, *b*₁₃ 160–3°; *d*₁₅ 1.0288.

EtNHPS(OEt)₂, *b*₁₂ 94°.^{511c}

- PrNHPS(OEt)₂, b₁₁ 98°; d₁₅ 1.005.^{511c}
i-BuNHPS(OEt)₂, b₁₂ 104°.^{511c}
 MeNHPS(OC₆H₄Cl-*p*)₂, d₂₈ 1.26; n 35/D 1.5356.^{524c}
 EtNHPS(OC₆H₄Cl-*p*)₂, d₂₈ 1.15; n 35/D 1.5290.^{524c}
i-PrNHPS(OC₆H₄Cl-*p*)₂, d₁₉ 1.13; n 35/D 1.5250.^{524c}
 AmNHPS(OC₆H₂Cl₃-2,4,6)₂, d₃₁ 1.07; n 35/D 1.4956.^{524c}
c-HexNHPS(OC₆H₂Cl₃-2,4,5)₂, m.66–72°.^{524c}
i-PrNHPS(OC₆H₂BrCl₂-4,2,6)₂, d₃₀ 1.23; n 35/D 1.5103.^{524c}
 EtNHPS(OC₆HCl₄-2,3,4,6)₂, d₃₀ 1.22; n 35/D 1.5608.^{524c}
 EtNHPS(OC₆Cl₅)₂, d₃₀ 1.36; n 35/D 1.5536.^{524c}
 PhNHPS(OPh)₂, m.92°.^{39a}
 PhNHPS(OC₆H₄Me-*p*)₂ m.106°.^{39a}
 Me₂NPS(OEt)₂, b₄₅ 107°.^{511c}
 Et₂NPS(OEt)₂, b₂₀ 110°; d₁₅ 1.0056.^{511c}
 Et₂NPS(OPh)₂, m.58°.^{39a}
i-Am₂NPS(OMe)₂, b₁₃ 118–21°; d₁₅ 1.0024.^{511c}
 Me₂NPS(OC₆H₄Cl-*p*)₂, d₂₄ 1.16; n 35/D 1.5583.^{511c}
 Et₂NPS(OC₆H₄Cl-*p*)₂, d₂₈ 1.16; n 35/D 1.5458.^{524c}
 Me₂NPS(OC₆H₂Cl₃-2,4,5)₂, d₃₁ 1.35; n 35/D 1.5737.^{524c}
 Et₂NPS(OCH₂)₂, b₃ 133–4.5°; d 20/0 1.1825; n 20/D 1.5050.²⁵
 Me₂NPS(OEt)OC₆H₄NO₂-*p*, m.133°.⁵²⁵
 Et₂NPS(OEt)OC₆H₄NO₂-*p*, n 25/D 1.5368.⁵²⁵
 H₂NPS(OPh)₂, m.115°.^{39a} 112°.²²⁶
 H₂NPS(OC₆H₄Cl-*p*)₂, m.96°.^{39a}
 H₂NPS(OC₆H₄Me-*p*)₂, m.131°.^{39a}
 (H₂N)₂PSOPh, m.119°.^{39a}
 (Et₂N)₂PSOEt, b.149–51°.^{511c}
 (PhNH)₂PSOPh, m.126°.^{39a}
 (H₂NNH)₂PSOPh, m.95°.⁶⁸⁷
 (H₂NNH)₂PSOC₆H₄Me-*p*, m.106°.⁶⁸⁷
 (EtNH)₃PS, m.68°.^{511c}
 (PrNH)₃PS, m.73°.^{511c} 74°.¹¹²
 (*i*-BuNH)₃PS, m.78.5°.^{511c}
i-BuNH(EtNH)₂PS, m.48.5°.^{511c}
 (PhNH)₃PS, m.154°.^{41, 112}
 (*o*-MeC₆H₄NH)₃PS, m.134.5°.⁶¹⁴
 (*p*-MeC₆H₄NH)₃PS, m.186°.⁴¹ 185°.⁶¹⁴
 (*p*-EtOC₆H₄NH)₃PS, m.152°.⁴¹
 (*p*-ClC₆H₄NH)₃PS, m.226°.¹¹²
 (PhCH₂NH)₃PS, m.126°.¹¹²

EtN:PSNH₂Et, m.169°. ⁵¹²

PrN:PSNHPr, m.152°. ⁵¹²

i-BuN:PSNHBu-*i*, m.150°. ⁵¹²

Acid-Esters and Derivatives

Acid-Esters, (RO)₂PSSH

(MeO)₂PSSH, b_{4.5} 62–3°; d₂₀ 1.2888; n 20/D 1.5343. ^{393b}

(EtO)₂PSSH, b₂ 80–2°, ⁴⁹¹ b_{4.5} 85–90°, ^{490c} b₅ 81.5–2.5°, ^{393b} b₁₂ 97–8°; ^{393a} d 13/4 1.1753, ⁴⁹¹ d₂₀ 1.1650, ^{393a} 1.1654; ^{393b} n 13.7/D 1.5119, ⁴⁹¹ n 20/D 1.5105, ^{393a} 1.5076. ^{393b}

(PrO)₂PSSH, b₂ 81.5–2.5°, ^{393b} 108°, ⁴⁹¹ b₃ 85–6°; ^{393a} d 13/4 1.1025, ⁴⁹¹ d₂₀ 1.1040; ^{393a} n 13.7/D 1.50176, ⁴⁹¹ n 20/D 1.4986, ^{393b} 1.4987. ^{393a}

(*i*-PrO)₂PSSH, b_{1.5} 82–5°, ⁴⁹¹ b₃ 70.5–1.5°, ^{393a} 71–2°; ^{393b} d 13/4 1.0920, ⁴⁹¹ d₂₀ 1.0911, ^{393b} 1.0913; ^{393a} n 13.7/D 1.49317, ⁴⁹¹ n 20/D 1.4920, ^{393a} 1.4918. ^{393b}

[Me₂C(NO₂)CH₂O]₂PSSH, m.103.8–4°. ³⁹⁹

Melting Points of Some Salts

Salts of (RO)₂PSSH

Me Ni, m.113°, ^{492a} 125°. ^{393b}

Et Ni, m.105°; Co, m.140; Fe¹¹¹, m.129°; ^{492a} K, m.157°; Pb, m.74°, ⁵⁰² 76°. ^{393a}, ^{393b}, ^{393c}

i-Pr Pb, m.131°. ^{393b}

Bu Hg, m.62°, ⁵⁰² 61°. ^{393b}

i-Bu Ni, m.63°. ^{492a}

Ph Ni, m.130. ^{492a}

Silver Salts of (RO)₂POSH

(MeO)₂ POSAg, m.144°. ²²⁴ (PrO)₂ POSAg, m.124°. ^{565c}

(EtO)₂ POSAg, m.82°. ^{565a}, ^{565b} (*i*-BuO)₂ POSAg, m.160°. ^{565c}

Ester-Anhydrides and Ester-Sulfides

(EtO)₂PO·O·PS(OEt)₂, b₃ 147.5–8.5°; d 0/4 1.2065, d 20/4 1.1885; n 20/D 1.4508. ²¹

(MeO)₂PS·O·PS(OMe)₂, b₂ 118–20°. ²³⁵

(EtO)₂PS·O·PS(OEt)₂, b_{0.2} 110–3°; d 25/4 1.189; n 25/D 1.4753. ⁷⁰⁷

(PrO)₂PS·O·PS(OPr)₂, n 25/D 1.4713. ⁷⁰⁷

(*i*-PrO)₂PS·O·PS(OPr-*i*)₂, d 25/4 1.093; n 25/D 1.4620. ⁷⁰⁷

$(\text{BuO})_2\text{PS}\cdot\text{O}\cdot\text{PS}(\text{OBu})_2$, $d_{25/4}$ 1.068; $n_{25/D}$ 1.4690.⁷⁰⁷
 $(\text{EtO})_2\text{PS}\cdot\text{S}\cdot\text{PS}(\text{OEt})_2$, b_2 88–90°. ⁴⁹¹
 $(\text{MeO})_2\text{PS}\cdot\text{S}_2\cdot\text{PS}(\text{OMe})_2$, m .52°. ^{393b}
 $(\text{EtO})_2\text{PS}\cdot\text{S}_2\cdot\text{PS}(\text{OEt})_2$, b_2 170–2°. ⁴⁹¹
 $(i\text{-PrO})_2\text{PS}\cdot\text{S}_2\cdot\text{PS}(\text{OPr-}i)_2$, m .92°. ^{393b}
 $(\text{EtO})_2\text{PS}\cdot\text{S}_3\cdot\text{PS}(\text{OEt})_2$, m .72°. ⁴⁹¹
 $(\text{EtO})_2\text{PS}\cdot\text{S}_4\cdot\text{PS}(\text{OEt})_2$, m .43°. ⁴⁹¹

Alkyl Phosphorus Compounds

EtPSCl_2 , b_{50} 80–2°; d_{20} 1.3606. ³¹⁴
 PrPSCl_2 , b_{50} 95–8°; d_{20} 1.2854. ³¹⁴
 $i\text{-BuPSCl}_2$, b_{50} 110–3°; d_{20} 1.2515. ³¹⁴
 $i\text{-AmPSCl}_2$, b_{50} 130–2°; d_{20} 1.1771. ³¹⁴
 $\text{EtPO}(\text{OEt})\text{SEt}$, b_4 76–6.5°; d_{20} 1.0709; $n_{20/D}$ 1.4730. ^{398c}
 $\text{EtPS}(\text{OEt})_2$, $b_{13.5}$ 82–3.5°; d_{20} 1.0332; $n_{20/D}$ 1.4563. ^{398c}
 $i\text{-AmPS}(\text{OEt})_2$, b . 250–5°; d_{20} 0.9848. ³¹⁴
 $\text{PhCH}_2\text{PS}(\text{OEt})_2$, $b_{3.5}$ 124–5°; d_{20} 1.1022; $n_{20/D}$ 1.5303. ^{398c}
 $\text{EtO}_2\text{CCH}_2\text{PS}(\text{OEt})_2$, b_5 105–6°; d_{20} 1.1204; $n_{20/D}$ 1.4621. ^{398c}
 $c\text{-C}_6\text{H}_9\text{PS}(\text{OMe})\text{SMe}$, $b_{3.5}$ 133°; $d_{25/4}$ 1.170. ²³⁶

Tetrathio-Orthoesters

The compounds, $\text{E}(\text{SR})_4$, in which E is an element of the fourth group, are esters rather than mercaptides.

TETRATHIO-ORTHO CARBONATES, $\text{C}(\text{SR})_4$

These are not well known. The tetraethyl was supposed to have been prepared from carbon tetrachloride and sodium mercaptide, ^{430b} but this was a mistake. This and others have been made from the isothioureas. Several have been recorded: ⁴⁸

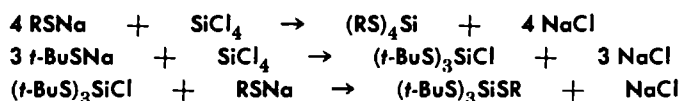
$(\text{MeS})_4\text{C}$, b_{12} 126–7°, m .65°; tetrabromide, $(\text{MeS})_2\text{C}(\text{SBr}_2\text{Me})_2$, decomposes at 122°.
 $(\text{EtS})_4\text{C}$, m .33.5°; tetrabromide, m .67.5°.
 $(i\text{-PrS})_4\text{C}$, m .61.4°.
 $(\text{C}_6\text{H}_{11}\text{S})_4\text{C}$, cyclohexyl, m .169°.

Several aromatic tetrathio-orthocarbonates have been obtained from nitrosoisothioureas. ³¹

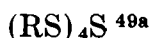
It has not been found possible to oxidise these tetrathio compounds to the tetrasulfones, ^{44a} but partial oxidation products, such as $(\text{MeS})_2\text{C}(\text{SO}_2\text{Ph})_2$ and $\text{MeS}(\text{PhS})\text{C}(\text{SO}_2\text{Ph})_2$, have been obtained indirectly. ^{44b}

TETRATHIO-ORTHOSILICATES, $\text{Si}(\text{SR})_4$

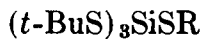
From silicon tetrachloride and sodium mercaptides, a number of tetrathioesters of orthosilicic acid, $\text{Si}(\text{SR})_4$, have been prepared: 46, 49a, 429b



The properties of some of the compounds follow. X-ray analysis shows that $(\text{BuS})_3\text{SiSCHMe}_2$ is isomorphous with $(\text{BuS})_4\text{Si}$.⁴²⁸

Properties of Tetraalkyltetrathio-Orthosilicates

Me, m.31°; b_{12} 144–6°; d 35/4 1.1888; n 35/D 1.5989.
 Et, m.–5.8°; b_{12} 169–71; d 25/4 1.0860, d 35/4 1.0785; n 25/D 1.5638, n 35/D 1.5591.
 Pr, b_{17} 204–6°; d 25/4 1.0328, d 35/4 1.0252; n 25/D 1.5431, n 35/D 1.5379.
i-Pr, m.33.5°; b_{13} 176–8°; d 35/4 1.0099; n 35/D 1.5350.
 Bu, b_4 210°; d 25/4 0.9958; n 25/D 1.5292.
i-Bu, b_4 183°; d 25/4 0.9886; n 25/D 1.5255.
s-Bu, b_4 182°; d 25/4 1.0022; n 25/D 1.5354.
t-Bu, m.161°, ^{49a, 429b} tetragonal, sublimes 160–5° at 4 mm.
 Am, b_4 230–1°.
 Cetyl, m.51°.
 Cyclohexyl, m.102.5°.
 Ph, m.115°.
p-Tolyl, m.129°.
p-Me₃CC₆H₄–, m.186°.



Me, m.44°; ^{49a, 429b} b_4 159–60°. ^{49a}	<i>s</i> -Bu, m.80°. ^{429b}
Et, m.27°; ^{49a, 429b} b_4 163–4°. ^{49a}	<i>t</i> -Am, m.114°. ^{46, 429b}
Pr, m. 62.5°. ^{49a, 429b}	<i>s</i> -Pentyl, m.29°; b_2 169–70°. ⁴⁶
<i>i</i> -Pr, m.105°; ^{49a, 429b} b_4 161–3°. ^{49a}	Cyclopentyl, m.105°. ^{46, 429b}
Bu, b_1 153.3–3.5°. ^{46, 429b}	Cyclohexyl, m.65°. ^{46, 429b}
<i>i</i> -Bu, m.77.5°; ^{46, 429b} b_1 146–8°. ⁴⁶	

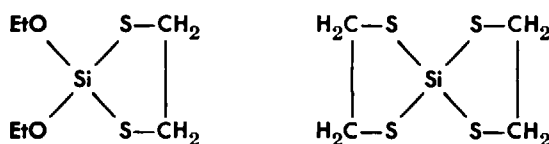
Halides

Si(ESMe₃)₃Cl, m. 71°;^{46, 49a} 71.5°; b₄ 145–50°.^{49a}
 Si(SMe)₃Br, b₁ 80–1°; d 25/4 1.4945; n 25/D 1.5658.^{74b}
 Si(SEt)₃Br, b_{2.5} 155–8°; d 25/4 1.3469; n 25/D 1.5650.^{74b}
 Si(SPr)₃Br, b_{1.5} 136–8°; d 25/4 1.2408; n 25/D 1.5418.^{74b}
 Si(SCHMe₂)₃Br, b_{2.5} 132–4°; d 25/4 1.2209; n 25/D 1.5410.^{74b}
 Si(SCH₂CHMe₂)₃Br, b₁ 143–4°; d 25/4 1.1789; n 25/D 1.5282.^{74b}
 Si(SCMe₃)₂Cl₂, b₁₃ 133.5–5.0°; n 16/D 1.522.⁴⁶
 Si(SEt)₂Br₂, b_{2.5} 115.0–5.5°; d 25/4 1.6493; n 25/D 1.5658.^{74b}
 Si(SCH₂CHMe₂)₂Br₂, b_{3.5} 76–9°; d 25/4 1.3527; n 25/D 1.497.^{74b}
 Si(SCMe₃)Cl₃, b. 174–7°.⁴⁶

Miscellaneous

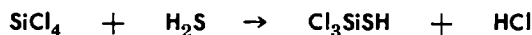
(*t*-BuS)₂Si(SCHMe₂)₂, m. 62.5°; b₂ 147–8°.⁴⁶
t-BuSSi(SCHMe₂)₃, m. 23.5°; b₃ 160–2°.⁴⁶
i-Pr trithio-orthosilicate, m. 56°; b₅ 183–6°.⁴⁶
 (*t*-BuS)₃SiOH, m. 91°.^{49a}
 [(*t*-BuS)₃Si]₂O, m. 249°.^{49a}
 (EtO)₃SiSH, b. 164–7°.²⁵⁴

Cyclic esters have been prepared from ethanedithiol, 2,2-diethoxy silicodithiolane, b₁₉ 129°; d 20/4 1.1344; n 20/D 1.4956; and the spiro diethylene ester:⁴⁵

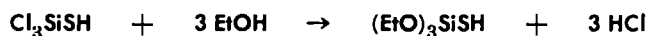


Mixed oxygen-sulfur esters can be made from the ester-chlorides, RO₂SiCl₂, (RO)₂SiCl₂ and (RO)₃SiCl.⁵⁴³

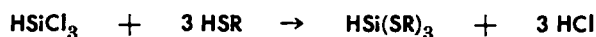
Silicon tetrachloride and hydrogen sulfide react:



With an alcohol, a trialkoxysilicon hydrosulfide is formed:²⁵⁴



What may be called trialkyltrithio-ortho-silicoformic esters, HSi(SR)₃, have been made from trichlorosilane and mercaptans in the presence of a base:^{74b}

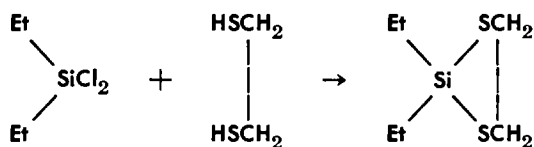


With benzoyl chloride, one alkylmercapto group of trialkylmercaptosilane is exchanged for chlorine:



In bromination, either the hydrogen atom or an alkyl mercapto group or both are replaced by bromine. The products may be: $(\text{RS})_3\text{SiBr}$, $\text{HSi(SR)}_2\text{Br}$ and $(\text{RS})_2\text{SiBr}_2$.⁷⁴⁶ Properties of some of $(\text{RS})_3\text{SiBr}$, $(\text{RS})_2\text{SiBr}_2$, and of $\text{HSi(SR)}_2\text{Br}$ will follow.

Mono and dialkyl silicon derivatives have been made from the corresponding chlorides in the usual way. Dialkylsilicon dichlorides react with ethanedithiol to give 2,2-dialkylsilico-1,3-dithiolanes:



The products are claimed to be heat stable and useful in lubricants.⁵⁹⁹ A mixed compound such as $\text{Me}_2\text{Si(SPh)SAm}$, may be made. Trialkylsilicon derivatives, such as Pr_3SiSPh , are known.⁴⁵¹ Some of these compounds are listed in the following pages.

Silicon sulfide reacts like carbon disulfide in the formation of a xanthate: ^{182a}



This product and the alkali salts of monoesters of di- or tri-thiometasilicic acid are claimed as flotation agents.^{183b}

Some Mixed Silicon Compounds

Trialkylmercapto Silanes

HSi(SMe)_3 , $b_{1.5}$ 66.5–9°, b_7 90–1°; $d_{25/4}$ 1.1423; $n_{25/D}$ 1.5761.⁷⁴⁶

HSi(SEt)_3 , b_1 87.5–8°, b_3 104–5°; $d_{25/4}$ 1.0484; $n_{25/D}$ 1.5440.⁷⁴⁶

HSi(SPr)_3 , b_1 120–1°, b_2 135°; $d_{25/4}$ 0.9991; $n_{25/D}$ 1.5278.⁷⁴⁶

$\text{HSi(SCHMe}_2)_3$, $b_{2.5}$ 100°, b_6 130°; $d_{25/4}$ 0.9864; $n_{25/D}$ 1.5221.⁷⁴⁶

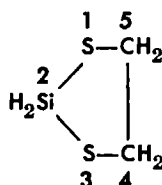
HSi(SBu)_3 , b_9 180–2°; $d_{25/4}$ 0.9819; $n_{25/D}$ 1.5160.⁷⁴⁶

$\text{HSi(SCH}_2\text{CHMe}_2)_3$, b_3 135–8°; $d_{25/4}$ 0.9694; $n_{25/D}$ 1.5160.⁷⁴⁶

$\text{HSi(SCMe}_3)_3$, m .48°; b_4 116–20°.⁷⁴⁶

$\text{HSi}(\text{SEt})_2\text{Cl}$, $b_{2.5}$ 63–4°; d 25/4 1.1218; n 25/D 1.5160.⁷⁴⁶
 $\text{HSi}(\text{SBu})_2\text{Cl}$, b_6 119°; d 25/4 1.0358; n 25/D 1.5030.⁷⁴⁶
 $\text{HSi}(\text{SCMe}_3)_2\text{Cl}$, b_4 78–80°; d 25/4 1.0222; n 25/D 1.5040.⁷⁴⁶
 $\text{HSi}(\text{SMe})_2\text{Br}$, b_8 70–2°; d 25/4 1.4997; n 25/D 1.5660.⁷⁴⁶
 $\text{HSi}(\text{SEt})_2\text{Br}$, b_8 81–4°; d 25/4 1.3677; n 25/D 1.5408.⁷⁴⁶
 $\text{HSi}(\text{SCHMe}_2)_2\text{Br}$, b_2 83–5°; d 25/4 1.2683; n 25/D 1.5195.⁷⁴⁶
 $\text{HSi}(\text{SCH}_2\text{CHMe}_2)_2\text{Br}$, $b_{3.5}$ 121–5°; d 25/4 1.2445; n 25/D 1.5159.⁷⁴⁶

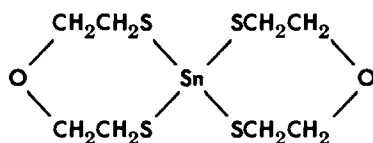
Silicodithiolane



2,2-Dimethyl-, b_2 54°; d 20/4 1.1077; n 20/D 1.5571.⁵⁹⁹
 2,2-Diethyl-, b_5 78–80°; d 20/4 1.0524; n 20/D 1.5350.⁵⁹⁹

TETRATHIOSTANNATES, $\text{Sn}(\text{SR})_4$

Stannic mercaptides can be prepared by the action of tin and hydrochloric acid on alkyl disulfides; from stannous chloride, a mercaptan, and air, or from stannic chloride and a mercaptan. $\text{Sn}(\text{SC}_6\text{H}_4\text{NMe}_2)_4$ melts at 159°.⁷⁵⁰ Many have been synthesized by methods similar to those used for the tetrathio-orthosilicates.^{47, 430a, 430b} The properties of some of these are in Table 4.3. The allyl and isobutenyl derivatives are liquids which polymerize. From 2,2'-dimercaptoethyl ether, a spiro compound, m.124°, has been prepared:

TETRATHIOGERMANATES, $\text{Ge}(\text{SR})_4$

From germanium tetrachloride, compounds of the general formula $\text{Ge}(\text{SR})_4$ have been obtained.^{49b} Their properties are listed in Table 5.3. Tetratertiarybutylmercapto germanium is tetragonal and isomorphous with the corresponding silicon and tin compounds.^{429a}

TABLE 4.3

*Properties of Tetrathio-orthostannates, Sn(SR)₄*⁴⁷

R	m. °C.	b _{0.001} °C.	n _{20/D}
Me	31	81	—
Et	—	105	1.6188
Pr	—	123	1.5851
<i>i</i> -Pr	—	92	1.5789
<i>n</i> -Bu	—	136	1.5539
<i>i</i> -Bu	—	126	1.5599
<i>s</i> -Bu	—	111	1.5668
<i>t</i> -Bu	188, ⁴⁷ 185.5–7 ^{666b}	—	—
<i>n</i> -Am	—	162	1.5475
<i>t</i> -Am	44	—	—

Lauryl m.35.5°. Cetyl m.53.5°. Cyclohexyl m.54°. Phenyl m.67°.

TABLE 5.3

Properties of Tetrathio-orthogermanates, Ge(SR)₄^{49b}

R	b. °C.	Pressure mm.	d 25/4	n 25/D
Me	138–40	4	1.4364	1.6379
Et	165	5	1.2574	1.5886
Pr	191–2	5	1.1662	1.5612
<i>i</i> -Pr	162–4	4	1.1478	1.5535
Bu	222–3	5	1.1072	1.5439
<i>i</i> -Bu	199–200	5	1.0984	1.5381
<i>s</i> -Bu	200–1	5	1.1119	1.5497

t-Bu, m.172–3°.*t*-Am, b 240–1°.^{49a}Cetyl, m.50–1°.^{49a}Cyclohexyl, m.84° and 88°.^{49a}O(CH₂CH₂S)₂Ge(SCH₂CH₂)₂O, m.159.5°.Ph, m.101.5°.^{49a}*p*-Tolyl, m.111°.^{49a}*p*-Me₃CC₆H₄-, m.156°.^{49a}*(t*-BuS)₃GeCl, m.67°; b₄ 156–7°.^{49a}

ALKYL THIOSULFATES

The alkyl thiosulfates have been studied extensively. The first objective was to get light on the constitution of thiosulfuric acid and its salts. It was soon found that alkyl thiosulfates are useful intermediates for the preparation of mercaptans and their derivatives. The reactions of various alkyl halides with metal thiosulfates, under different conditions, have been of considerable theoretical interest.

Bunte, for whom the salts are named, caused ethyl bromide to react with sodium thiosulfate in an effort to decide between the two possible structures of thiosulfuric acid, $\text{O}_2\text{S}(\text{ONa})\text{SNa}$ and $\text{OS}_2(\text{ONa})_2$, assuming that sodium joined to sulfur would be replaced more rapidly. He obtained the ester-salt, $\text{EtS}_2\text{O}_3\text{Na}$, which, on hydrolysis with hydrochloric acid, gave ethyl mercaptan and enough sulfuric acid to account for half of the original sulfur. Whether this showed anything as to the constitution of the sodium thiosulfate is questionable, but the Bunte salts have been most useful.¹¹⁵ The fact that ethyl potassium thiosulfate was obtained from ethyl bromide and sodium potassium thiosulfate was taken as showing that this salt is $\text{KO}\cdot\text{SO}_2\cdot\text{SNa}$. Actually it proved that the potassium ester salt, EtKS_2O_3 is less soluble than the sodium, EtNaS_2O_3 .⁶³⁸ Similar results were obtained with potassium ammonium thiosulfate.²⁴⁴

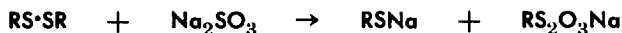
The methyl, propyl, and isobutyl thiosulfates were prepared, but chloroform, iodoform and carbon tetrachloride did not react as expected.⁶⁶⁹ Allyl, *i*-propyl, hydroxyethyl, and ethylene salts were obtained later. Ethyl chloroacetate and chloroacetic acid gave the salts, $\text{EtO}_2\text{CCH}_2\text{S}_2\text{O}_3\text{Na}$ and $\text{NaO}_2\text{CCH}_2\text{S}_2\text{O}_3\text{Na}$.⁵⁸⁰

Ethyl thiosulfuric acid, $\text{EtS}\cdot\text{SO}_3\text{H}$, is said to have been made from ethyl sulfide and sulfuric acid.⁶⁶² This statement was made in 1869 and needs verification. It is known that ethyl sulfide is quite soluble in sulfuric acid. Phenyl mercaptan unites with pyridinesulfur trioxide to give the pyridine salt of phenylthiosulfuric acid.^{64a, 64b, 190} A mercaptan, iodine and sodium sulfite unite to form the thiosulfate.⁶⁶⁸ Formaldehyde unites with thiosulfuric acid to form a sort of hemiformal. This decomposes reversibly:



This reaction is monomolecular. The thioformaldehyde is precipitated as the trimer.⁶²⁵

An alkyl disulfide reacts with sodium sulfite to produce a thio-sulfate: ⁶²⁹



According to a later study, it is better to use the bisulfite as the sulfite is too alkaline. Some Bunte salts not otherwise available can be made in this way. The reaction is more complicated than as written. Some alkali thiosulfate is also formed.⁴⁵⁵ In the case of aminoaryl disulfides, and with these only, sulfur dioxide may be substituted for the salt.^{144, 482}

Many studies have been made on the rates of formation of alkyl thiosulfates. Methyl iodide, bromide and chloride, ethyl iodide and bromide, and ethylene iodide, bromide-iodide, bromide, chloride-bromide and chloride-iodide have been compared as to their reaction rates.^{211, 648} The data are in agreement with theory.^{518a} The velocity with methyl bromide is seventeen times as great as calculated from the collision theory in its simplest form.^{518b} The energies of activation increase in inverse order to the heats of the reactions with various alkyl halides.⁵³⁹ The reaction with sodium chloracetate is bimolecular,⁴⁴¹ so is that with dichloroethyl ether.⁶² The velocity of the reaction between the bromoacetate ion and sodium thiosulfate has been measured from 30 to 90°. ^{397a, 398} The effect of concentration has been determined.^{446a} The α - and β -bromopropionates have been compared.^{448a} Bromomalonic and bromosuccinic acids have been studied also.^{67, 68, 478} There have been extensive investigations on the effects of neutral salts,^{72, 73, 425, 446b, 447, 448b} of nonelectrolytes ^{217, 240, 396, 397b 423, 685} and of changing the reaction medium.^{424, 620} Bunte salts, $\text{H}_2\text{NCH}_2\text{CH}_2\text{SSO}_3\text{Na}$,^{81, 89} $\text{HN}(\text{CH}_2\text{CH}_2\text{SSO}_3\text{Na})_2$,⁸¹ $\text{Et}_2\text{NCH}_2\text{CH}_2\text{SSO}_3\text{Na}$, $\text{MeNHCH}_2\text{CHPhSSO}_3\text{Na}$, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{SSO}_3\text{Na}$, $\text{MeNHCHMeCHPhSSO}_3\text{Na}$, and many other similar salts have been prepared from β -haloethylamines.⁸⁹ Thallium thiosulfate has been recommended for the preparation of such salts.⁴⁵⁵

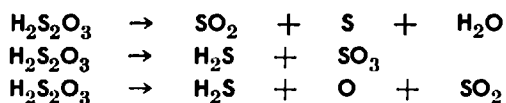
Bunte salts are readily prepared from alkyl halides or sulfates and sodium thiosulfate. This salt, $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$, m. wt. 248, is soluble in about half of its own weight of water at 50°. The alkyl halides, except the lower ones and those that have solubilizing

groups in them, are only slightly soluble in water and still less so when a large amount of an inorganic salt is present. Usually the thiosulfate is dissolved in 2 or 3 parts of water and the alkyl halide, in more or less alcohol, is added dropwise with stirring and heating under reflux. The completion of the reaction may be judged by the disappearance of the alkyl halide or by the absence of a precipitate of sulfur when a mineral acid is added to a test portion of the solution. On account of the instability to heat of sodium thiosulfate and its derivatives, too high a temperature and too long a time of heating are to be avoided. The less soluble Bunte salts separate out on cooling and may be recrystallized from methanol or ethanol. The more soluble ones may be recovered by evaporating the reaction mixture to dryness and extracting the residue with boiling alcohol.^{551c} Ethyl bromide and thiosulfate solution, shaken together at 35°, give an almost theoretical yield of the salt.⁵⁵² Ethylene bromide and a saturated aqueous solution of sodium thiosulfate, stirred together for 10 days at 40°, give a good yield of the desired salt.⁴⁸⁹ Secondary and tertiary alkyl bromides give poorer yields on account of the formation of olefins.²⁷⁴ Commonly the Bunte salts are prepared as intermediates and used for further reactions in the solutions in which they are formed. In such cases, their isolation is unnecessary.

The methyl Bunte salt crystallizes from water with one half of a molecule of water of crystallization.⁶⁶⁹ This is true also of the ethyl, amyl, and hexyl.⁵⁵³ The ethylene, hexamethylene, and decamethylene have two molecules of water and the pentamethylene, three.⁵⁵⁵ The crystal structure²⁴⁴ and diamagnetic susceptibility^{149a} have been studied.

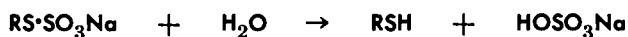
Reactions of Alkyl Thiosulfates

Thiosulfuric acid decomposes in three ways: ^{317a}

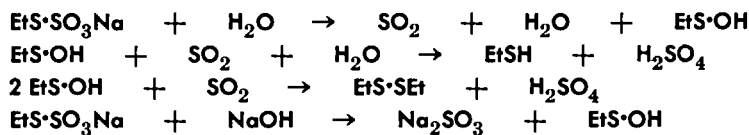


When a dilute solution of sodium thiosulfate is added slowly to boiling hydrochloric acid, 91% goes to hydrogen sulfide and sulfuric acid.²⁴⁵ Ethyl thiosulfate is unlike sodium thiosulfate in that it does not decolorize cupric salts and does not dissolve silver

chloride,^{317a} but its hydrolysis follows the same pattern. As the sulfur-carbon bond is not easily broken, EtSH will take the place of HSH and EtS-, which doubles up to EtS·SEt, will be found instead of S. Hydrolysis in the presence of acid is usually written: ^{115, 580}



Another view is: ^{64a, 261a, 317b, 317c, 612a}



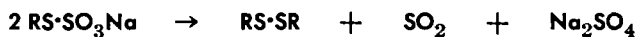
The existence of EtSOH, the assumed intermediate, has been questioned,^{573b, 574a, 574b} but tangible evidence of its presence has been brought forward.¹⁹⁰ A good yield of mercaptan may be obtained by acid hydrolysis.^{43c, 346a, 442, 573b, 574a, 574b, 580} The presence of a reducing agent aids its formation.^{317a} The alkaline hydrolysis of benzyl sodium thiosulfate gives several products, among which are benzyl disulfide, sodium thiobenzoate and benzoate.^{262, 573b, 574b, 574c} The addition of sodium carbonate, or hydroxide, to a nitrobenzyl thiosulfate causes the separation of the disulfide.^{573c}

At 100° an alkyl thiosulfate decomposes into the disulfide and sodium dithionate: ^{115, 551c, 552, 689}



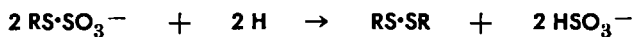
When heated for some time, methyl sodium thiosulfate goes to pieces and methyl sulfide, methyl disulfide and sulfur dioxide are given off. At 200° methyl sulfone, Me₂SO₂, sublimes.⁷⁸

Dry distillation gives disulfide, sulfur dioxide, and sodium sulfate: ^{78, 580}

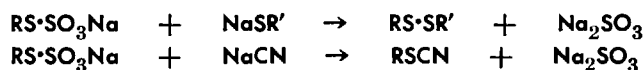


Benzoyl chloride and sodium thiosulfate, heated together in water-alcohol solution, gives a 58% yield of benzoyl disulfide (PhCOS)₂.^{730c}

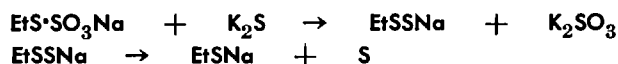
Electrolysis with a diaphragm gives the disulfide at the cathode: ^{573a}



The mercaptan from an alkyl sodium thiosulfate can be converted directly into derivatives without isolation. An aldehyde,^{289a, 683, 730a} or a ketone,^{54, 231b, 683} may react with the nascent mercaptan. A mercury mercaptide is obtained when ethyl sodium thiosulfate is treated with mercuric cyanide.^{318b} The reaction with a sodium mercaptide gives a disulfide and that with sodium cyanide, a thiocyanate:²⁴⁶



The addition of an alcohol solution of potassium sulfide to a like solution of ethyl sodium thiosulfate causes the separation of alkali sulfite. The solution turns yellow which is believed to be due to EtSSK. On heating, sulfur is deposited. The reactions seem to be:^{318a}



Ethylene sodium thiosulfate and sodium tetrasulfide give a polymeric ethylene tetrasulfide.^{371b}

Reduction with sodium results in mercaptan and sodium sulfite:⁶⁶⁸



2-Mercaptohydroquinone has been made by reducing the corresponding thiosulfate with zinc and hydrochloric acid.⁶

Oxidation with iodine,^{573d, 683, 730b} or hydrogen peroxide,^{683, 715, 730b} converts an alkyl thiosulfate to the disulfide. Stronger oxidation takes it to the sulfonic acid salt.^{342c} If this is done with chlorine in water the product may be the sulfone chloride or the sulfonate, according to conditions.^{192, 195}

An alkyl thiosulfate reacts with phosphorus pentachloride to give an unstable chloride:^{551c, 668}



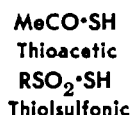
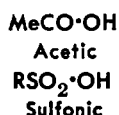
The silver salt with phosphorus trichloride goes to the alkyl disulfide and phosphorus oxychloride.⁵⁸⁴

It has been proposed to use the thiosulfate group as the water-soluble end in wetting, cleansing and dispersing agents. Sodium thiosulfate may be caused to react with a decyl or dodecyl halide,

with β -chloroethyl stearate, $C_{17}H_{35}CO_2CH_2CH_2Cl$,^{342b, 343} with a long-chain ester,^{342a, 344, 422} with an alpha-halogenated ether, such as $C_{12}H_{25}OCH_2Cl$ ¹⁸⁵ or $C_{16}H_{33}OCH_2Cl$,⁶⁶⁵ or with other similar halides to give useful products.^{185, 342d, 624, 665} The benzyl^{346b} and ethyl⁵³³ derivatives are said to be valuable in flotation.

ESTERS OF THIOSULFONIC ACIDS

A sulfonic and a thiosulfonic acid are formally related to each other as acetic and thioacetic.



The thiolsulfonic acids are not as well known as are their esters. The chief interest in these is in their isomerism with the disulfoxides:

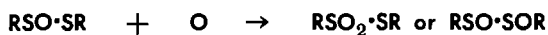


For quite a while there was uncertainty as to which of the two structures should be assigned to them. There is in any case only one compound. The aromatic compounds of this class have been investigated more thoroughly than the aliphatic. Esters, RSO_2SR' , in which the two radicals are different are known but are not so common as those in which both are the same.

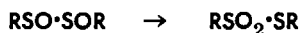
The oxidation of ethyl disulfide by dilute nitric acid^{438, 477, 479, 488, 556a, 556d} or by peracetic acid in ethyl acetate at 0° ^{649b} gives what might be supposed to be the disulfoxide, $EtSO\cdot SOEt$.



The oxidation of ethyl sulfide under comparable conditions gives ethyl sulfoxide, Et_2SO . Sulfoxides are comparatively unstable and are readily oxidised or reduced. This is true of sulfur dioxide and of quadrivalent sulfur compounds in general. If it is assumed that the first oxidation product is the mono-sulfoxide the second oxygen atom might go either to the $-SO-$ group or to the $-S-$ atom:

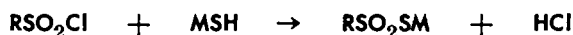


Or there might be disproportionation:



It is, of course, possible that this reaction may be reversible.

Ethane sulfonyl chloride and a metal sulfide may give various products according to conditions. A metal salt of an alkanethiosulfonic acid can be made from the sulfone chloride and a metal hydrosulfide: ⁵³

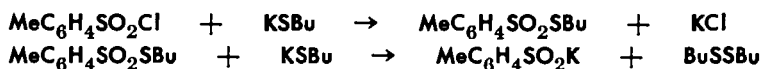


The ester, EtSO_2SEt , may be formed.^{649b} As the metal sulfide is a reducing agent, the ester may be regarded as an intermediate in the reduction of the sulfone chloride to the mercaptan. When the metal sulfide is added to the chloride, sulfur separates and then dissolves:



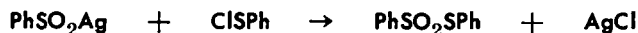
Alkylation with ethyl bromide gives the ester, EtSO_2SEt , $b_{0.2} 56^\circ$; $n_{25/D} 1.4972$,^{649b} which is identical with the above oxidation product.^{547c, 649b, 668} This is a general reaction.⁷⁵

Benzene and toluene thiosulfonic acids have been alkylated similarly.^{547b, 549, 551a, 551b} Toluene sulfone chloride reacts with a mercaptan in alkaline solution to give the ester.^{293, 391} This may react with a second molecule of the mercaptide: ²⁹³

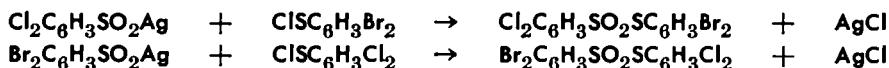


Benzenesulfone iodide and a silver mercaptide, AgSR , give much better yields of the esters.²⁹¹

A silver sulfinate and a sulfene chloride give the ester: ^{260a, 457, 759}



The unsymmetrical structure seems to be proved by the fact that two distinctly different but isomeric products are obtained when the $-\text{SO}_2\text{Ag}$ and $\text{ClS}-$ groups are interchanged: ^{291, 517}



2-Thienyl "disulfoxide" is formed from 2-thiophenesulfinic acid and hydriodic acid.¹⁷⁰ Benzenesulfinic acid is similarly reduced by hydrogen sulfide.^{547a} By a sort of disproportionation, three molecules of a sulfinic acid give one of the ester and one of the sulfonic acid:



This takes place when the sulfinic acid is heated in water solution.^{263a, 547a, 548, 551a, 551b, 556a, 556b} It goes on slowly at room temperature in a vessel protected from the air.^{556c}

In concentrated hydrochloric acid β -naphthalenesulfinic acid goes to the thiolsulfonate, $C_{10}H_7SO_2SC_{10}H_7$.⁴⁴⁵ An aryl sulfinic acid and benzoyl chloride give the "disulfoxide" and benzoic acid.^{361a} Camphor- β -sulfinic acid is readily converted to the "dicamphoryl- β - α -disulfoxide," m.212°; $[\alpha]$ 20/D -93.04.³⁴⁸

A disulfide takes up four atoms of bromine or four atoms of iodine. Hydrolysis of either of these gives the disulfoxide. Treatment of this with hydrobromic or hydriodic acid regenerates the tetrahalides.^{261b, 261c} It is somewhat simpler to assume the disulfoxide structure in writing these reactions, but it must be remembered that sulfur to sulfur and sulfur to halogen bonds are labile. The chlorination of benzyl mercaptan gives some of the thiolsulfonate along with the disulfide and sulfone chloride.¹⁹⁵

The facts that dibenzyl "disulfoxide," boiled with alcoholic potash, gives the disulfide and that dinaphthyl "disulfoxide" is reduced to the disulfide by sodium bisulfite have been considered as favoring the symmetrical formula, $RSO \cdot SOR$.^{350b, 350c} The above remarks apply here also. A study of the reactions of methyl-camphor-10-thiolsulfonate with a number of sodium sulfates has given evidence of the correctness of the unsymmetrical structure.²⁹⁰ A synthesis which points to the unsymmetrical structure is that from diphenyldiazomethane, sulfur dioxide and a mercaptan: ⁴³⁴



The infrared spectra of "disulfoxides" confirm the unsymmetrical structure.¹⁷¹ In x-ray studies, they have been compared with $(ArSO_2)_2$, $(ArSO_2)_2S$, $(ArSO_2)_2S_2$ and $(ArSO_2)_2S_3$.¹⁷⁵

The "disulfoxide" from the oxidation of cystine has received considerable attention.^{704, 706}

The reaction of methanesulfonyl chloride with *p*-methoxyphenyltellurium chloride gives $MeSO_2STeC_6H_4OMe$.^{249e} Treating sodium methanethiosulfonate with sulfur dichloride gives a compound having five sulfur atoms in a row, two of them oxidised:

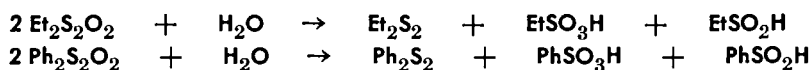


Analogous compounds having selenium and tellurium as central atoms, $(MeSO_2S)_2Se$ and $(MeSO_2S)_2Te$, have been made.^{249d}

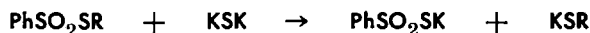
The crystal structures of these have been determined. They are isomorphous, each having four molecules in the unit cell.²⁵⁰

At 150° benzyl "disulfoxide" decomposes into benzyl sulfide and disulfide, benzaldehyde, benzyl acetate, and methyl phenylthioacetate.⁶⁶³

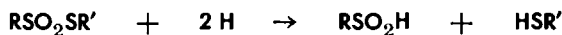
Alkaline hydrolysis gives sulfinic and sulfonic acids and disulfide: 350b, 547c, 549, 550, 551a, 551b, 556b, 556d



Potassium sulfide splits the ester: 549, 551a, 551b

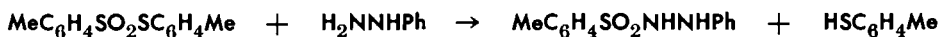


Reduction splits the ester into sulfinic acid and mercaptan: 317d, 517, 547b, 547c, 548, 556b, 556d



Further reduction converts the sulfinic acid to a mercaptan.^{547a, 547b, 549, 551a, 551b} Lithium aluminum hydride gives the disulfide and mercaptan.⁶⁸⁴ Sodium bisulfite reduces to the disulfide.^{350c}

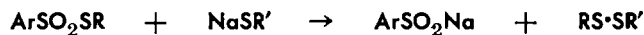
Hydroxylamine reacts with the *p*-tolyl "disulfoxide" in different ways according to conditions. *p*-Toluenesulfonamide may be formed. Phenylhydrazine displaces the mercaptan: 361b



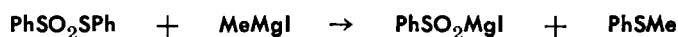
Chlorination converts a thiosulfonic ester to the sulfone chloride, RSO_2Cl .^{195, 550} Aryl esters, $\text{ArSO}_2\cdot\text{SAr}$, both phenyl and tolyl, have been brominated. There seems to have been only addition.^{547a, 548, 550} Oxidation leads to the sulfonic acid.^{556a, 556c}

The reaction with hydrobromic acid gives a sulfenyl bromide, ArSBr .^{260a}

A thiosulfonic ester and a mercaptide give a sulfinic salt and a disulfide: 293, 549, 556a, 556b, 556c, 650



Writing the thiosulfonic ester backward, $\text{RS}\cdot\text{SO}_2\text{Ar}$, makes it look like a sulfene halide, RSX , and brings this reaction in line with those of the sulfene halides. This is a satisfactory way to prepare unsymmetrical aryl disulfides.⁶⁵⁰ The reaction with a Grignard reagent is somewhat similar:



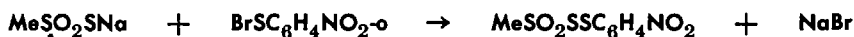
Some disulfide is a by-product.⁵¹⁷

The $-SR'$ group of a thiosulfonic ester can be substituted for an active hydrogen. Thus with malonic ester, the product is $R'SCH(CO_2Et)_2$.^{108, 289b} The $MeS-$ and $PhS-$ groups have been introduced into dibenzenesulfonylmethane in this way, giving $MeSCH(SO_2Ph)_2$, $(MeS)_2C(SO_2Ph)_2$, $PhSCH(SO_2Ph)_2$ and $PhS-(MeS)C(SO_2Ph)_2$.^{44b} 10,10-bis-Methylmercaptothioxanthene-5,5-dioxide has been prepared similarly.⁴³³ With ketosulfones, RSO_2CH_2COMe , there is a similar substitution and there may be also an exchange of the RSO_2- group of the thiosulfonic ester and that of the ketosulfone.¹⁶⁰

Methyl methanethiosulfonate and similar esters are claimed as selective solvents for extracting polycyclic hydrocarbons from petroleum fractions.⁷⁴⁵

Several selenium analogs, $o\text{-NO}_2C_6H_4SeSO_2R$, have been prepared. The melting points are: $R = \text{phenyl}$, 109° ; $p\text{-tolyl}$, 118° ; $o\text{-tolyl}$, 95° ; and $p\text{-bromophenyl}$, 126° .^{249a}

By causing $o\text{-nitrobenzenesulfonyl}$ bromide to react with a salt of an alkanethiosulfonic acid, compounds having an additional sulfur atom are obtained:



This melts at 98° and the ethane derivative at 91° .^{249b} Similarly, from the selenenyl bromide, $o\text{-NO}_2C_6H_4SeBr$, the ester, $MeSO_2SSeC_6H_4NO_2-o$, $m.p. 96^\circ$, has been prepared.^{249a}

The diamagnetic susceptibilities of the ethyl and $p\text{-tolyl}$ $p\text{-tolylthiosulfonates}$ are 114.9 and 156.7.^{149b}

THIOSULFINIC ESTERS

$RSO \cdot SR'$

Allicin, of which 6 g. has been obtained from 4 kg. of garlic cloves,¹³² has been found to have the structure $H_2C:CHCH_2SO \cdot SCH_2CH:CH_2$.¹³³ The fact that this shows antibacterial action led to the preparation of other compounds of this class. These are conveniently prepared by the oxidation of alkyl disulfides by means of peracids. The oxidation goes readily when the alkyls are primary, poorly when they are secondary, and not at all when they are tertiary. The formula, $t\text{-BuS} \cdot SOEt$, has been assigned to the oxidation product from the ethyl $t\text{-butyl}$ disulfide.^{134, 649a, 677} The benzyl ester has been prepared from benzyl disulfide and per-

benzoic acid. It is reduced back to the disulfide by sodium sulfite. When the reduction is by cysteine, the product may be a mixed disulfide.⁹⁰

The alkyl thiolsulfonates are mobile liquids, soluble in organic solvents. They are fairly stable at room temperature and can be distilled at low pressures. The properties of some of them are in Table 6.3. The derivative from the oxidation of allyl disulfide was found to be identical with the compound from garlic.

TABLE 6.3

Properties of Some Aliphatic Thiosulfinic Esters^{649a}

Formula	b. °C.	Pressure	d 20/4	n 25/D	Solubility in water
MeSO·SMe	64	0.5	1.222	1.5481	∞
EtSO·SEt	67	0.5	1.104	1.5244	11
PrSO·SPr	25-35	0.01	1.041	1.5098	2
<i>i</i> -PrSO·SPr- <i>i</i>	25-30	0.1	1.057	1.5090	2.5
<i>t</i> -BuSO·SEt	25-35	0.1	1.043	1.5092	3
C ₆ H ₅ SO·SC ₆ H ₅	—	—	1.109	1.5600	2.5
BuSO·SBu	20-30	0.00001	0.992	1.5041	0.1
AmSO·SAm	45	0.00001	0.988	1.4990	0.015

THIOSULFITE ESTERS

ROS·SOR

As H₂S₂O₃ is thiosulfuric acid, H₂S₂O₂ should be thiosulfurous. It has been so designated though the name does not fit the constitution. Only recently has the free acid been prepared by saponification of one of its esters under special conditions.⁶⁷²

The esters were discovered back in 1895⁴⁶⁴ and appear to have been forgotten for 40 years. They are not mercaptan derivatives but are mentioned here briefly since they are isomeric with thiosulfonic esters, RSO₂·SR, and bear a formal relationship to the sulfenic esters RS·OR.

These esters are prepared by the reaction of sulfur monochloride on sodium alcoholates, free from the alcohols, suspended in well cooled petroleum ether.^{509a, 671} The methyl ester, Me₂O₂S₂, boils at 34.2 to 34.7° at 17 mm. and the ethyl, at 62.0 to 62.7° at 15 to 16 mm.^{509a} They are stable in contact with water or air. Concentrated acids cause the separation of sulfur. Sodium ethyl-

ate, in absolute alcohol, abstracts sulfur from the ethyl ester, $S_2O_2Et_2$, leaving $S(OEt)_2$, $b_{17} 24^\circ$, which is oxidised by molecular oxygen to ethyl sulfite, $OS(OEt)_2$.^{510a} Potassium hydroxide, in methanol, causes the separation of sulfur and the formation of potassium thiosulfate.^{509b} The methyl ester is decomposed by dilute hydrochloric acid, yielding sulfur, pentathionic, sulfurous, and thiosulfuric acids.^{673b} Methyl and ethyl thiosulfites are decomposed when refluxed at atmospheric pressure. Hydrogen sulfide and sulfur are produced by both; the other products are methyl formate from the methyl ester and ethyl acetate from the other.^{509b}

Alkoxy determinations show the presence of $-OR$ groups in these esters.^{509b} The parachors of several have been measured and are given in Table 7.3 along with the densities and surface tensions.^{673a}

TABLE 7.3
Thiosulfite Esters, ROSSOR

Alkyl	d 25/4	Surface tension	Parachor
Dimethyl	1.1841	32.45	254.3
Diethyl	1.0815	29.53	332.4
Dipropyl	1.0361	29.16	408.7
Dibutyl	1.0031	28.82	485.6

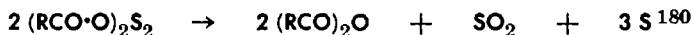
The results indicate the absence of homopolar bonds, but do not decide between the structures, $RO\cdot S\cdot S\cdot OR$ and $S:S(OR)_2$.^{673a} Raman spectra^{300, 622} and dipole moments⁶²² of the methyl and ethyl esters favor the structure, $RO\cdot S\cdot S\cdot OR$. The diamagnetic moments for the methyl and ethyl esters are 62.26 and 86.22.^{149a, 149b}

A silver salt of an organic acid and sulfur chloride react:



The product may be considered a mixed anhydride of the organic acid and $S_2(OH)_2$ of which S_2Cl_2 is the chloride. Compounds of this sort have been obtained from silver acetate, butyrate, *i*-buty-

rate, *i*-valerate, and palmitate. They are viscous unstable compounds. They decompose:



The amine sulfides, $(\text{R}_2\text{N})_2\text{S}_2$, are amides of the acid, $(\text{HO})_2\text{S}_2$. They are discussed in the chapter on substituted sulfides.

BIBLIOGRAPHY

1. C. E. Adams and W. A. Proell to S. O. of Indiana, U.S. pat. 2,573,674 (1951)—C.A. 46, 4026.
2. C. E. Adams and B. H. Shoemaker to S. O. of Indiana, U.S. pat. 2,372,244 (1945)—C.A. 40, 1029.
3. J. A. Adams, *J. Econ. Entomol.*, 42, 366–71 (1949)—C.A. 43, 9345.
4. J. W. Airan and S. V. Shah, *J. Indian Chem. Soc.*, 22, 359–63 (1945)—C.A. 40, 6455.
5. Max Albrecht, *Ann.*, 161, 129–48 (1872).
6. W. Alcalay, *Helv. chim. acta*, 30, 578–84 (1947)—C.A. 41, 4122.
7. Glen Alliger to Firestone Tire and Rubber Co., U.S. pat. 2,495,085 (1950); 2,581,921 (1952)—C.A. 45, 177; 46, 7581.
8. American Cyanamid Co., (a) Fr. pat. 665,179 (1928); (b) Brit. pat. 588,090 (1947); (c) 644,414 (1950)—C.A. 24, 814; 41, 7106; 45, 3862.
9. American Cyanamid Co., (a) Brit. pat. 646,188 (1950); (b) 672,663, 672,679 (1952)—C.A. 45, 5713; 47, 303.
10. American Cyanamid Co. (J. T. Cassaday), Ger. pat. 847,-897 (1954)—C.A. 48, 2084.
11. J. A. Anderson to S. O. Co. of Ind., U.S. pat. 2,316,089 (1943)—C.A. 37, 5858.
12. L. D. Anderson and J. W. Hashe, *J. Econ. Entomol.*, 42, 933–41 (1949)—C.A. 44, 3660.
13. L. D. Anderson and R. N. Hofmaster, *J. Econ. Entomol.*, 41, 278–82 (1948)—C.A. 42, 7918.
14. Ludwig Anschütz, W. Broeker, and Anna Ohnheiser, *Ber.*, 77, 439–46 (1944)—C.A. 40, 4358.
15. Ludwig Anschütz and Hans Walbrecht, *J. prakt. Chem.*, [2] 133, 65–80 (1932)—C.A. 26, 2437.
16. Richard Anschütz and W. O. Emery, *Ann.*, 253, 105–21 (1889).

17. E. W. Antnon, *J. Econ. Entomol.*, **42**, 854 (1949)—C.A. **44**, 1641.
18. J. W. Apple and G. C. Decker, *J. Econ. Entomol.*, **42**, 88–92 (1949)—C.A. **43**, 6354.
19. F. S. Arant, *J. Econ. Entomol.*, **41**, 803 (1948)—C.A. **43**, 1521.
20. A. E. Arbuzov, *J. Russ. Phys. Chem. Soc.*, **42**, 549–61 (1910)—C.A. **6**, 85.
21. A. E. Arbuzov and B. A. Arbuzov, *J. prakt. Chem.*, [2] **130**, 103–32 (1931)—C.A. **25**, 3618.
22. A. E. Arbuzov and G. K. Kamai, *J. Russ. Phys. Chem. Soc.*, **61**, 2037–42 (1929)—C.A. **24**, 5736.
23. A. E. Arbuzov and K. V. Nikonorov, (a) *Doklady Akad. Nauk SSSR*, **62**, 75–8 (1948); (b) *J. Gen. Chem. (USSR)*, **18**, 2008–15 (1948)—C.A. **43**, 1004, 3801.
24. A. E. Arbuzov and O. M. Shapshinskaya, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1952**, 842–6—C.A. **48**, 556.
25. A. E. Arbuzov and V. M. Zoroastrova, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1950**, 357–69; **1952**, 453–8, 789–800—C.A. **45**, 1512; **47**, 4833, 10461.
26. A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhenskii, *Bull. acad. sci. URSS, Cl. sci. chim.*, **1948**, 208–18—C.A. **42**, 4932.
27. B. A. Arbuzov and N. I. Rizpolozhenskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1952**, 854–64, 956–61—C.A. **47**, 9903, 9904.
28. B. A. Arbuzov and T. G. Shavsha, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1951**, 795–8—C.A. **46**, 3817.
29. B. A. Arbuzov and V. S. Vinogradova, *Bull. acad. sci. URSS, Classe sci. chim.*, **1947**, 459–72; *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1951**, 733–40; **1952**, 865–74—C.A. **42**, 3312; **46**, 7515; **47**, 10548.
30. C. S. Argyle and G. M. Dyson, *J. Chem. Soc.*, **1937**, 1629–34—C.A. **32**, 511.
31. Fritz Arndt, *Ann.*, **384**, 322–51 (1911); *ibid.*, **396**, 1–22 (1913)—C.A. **6**, 345; **7**, 1514.
32. P. M. Arnold to Phillips Pet. Co., U.S. pat. 2,574,457 (1951); 2,634,291 (1953)—C.A. **46**, 7581; **48**, 2768.
33. R. F. Ashbolt and Harold Coates to Albright & Wilson, Ltd., Brit. pat. 656,303 (1951)—C.A. **46**, 7581.
34. K. D. Ashley to Am. Cyanamid Co., U.S. pat. 2,343,213 (1944)—C.A. **38**, 4961.

35. G. W. Ashworth to Monsanto Chem. Co., U.S. pat. 2,268,467 (1941)—C.A. 36, 2567.
36. P. A. Asseff to Lubri-Zol Corp., U.S. pat. 2,261,047 (1941)—C.A. 36, 1174.
37. L. F. Audrieth and A. D. F. Toy, J. Am. Chem. Soc., 64, 1553-5 (1942)—C.A. 36, 5437.
38. W. Autenrieth and Heinrich Hefner, Ber., 58, 2151-6 (1925)—C.A. 20, 914.
39. W. Autenrieth and O. Hildebrand, (a) Ber., 31, 1094-1110 (1898); (b) *ibid.*, 1111-3.
40. W. Autenrieth and Wilhelm Meyer, Ber., 58, 840-7 (1925)—C.A. 19, 2325.
41. W. Autenrieth and P. Rudolph, Ber., 33, 2112-15 (1900).
42. P. R. Averell and M. V. Norris, Anal. Chem., 20, 753-6 (1948)—C.A. 42, 8714.
43. H. J. Backer, (a) Rec. trav. chim., 49, 1048-53 (1930); (b) *ibid.*, 50, 268-78 (1931); (c) *ibid.*, 51, 775-82, 988-90 (1932)—C.A. 25, 76, 2691; 26, 5546; 27, 491.
44. H. J. Backer, (a) Rec. trav. chim., 67, 894-906 (1948); (b) *ibid.*, 71, 409-19 (1952)—C.A. 43, 6995; 46, 11195.
45. H. J. Backer and W. Drenth, Rec. trav. chim., 70, 559-63 (1951)—C.A. 46, 5476.
46. H. J. Backer and H. A. Klasens, Rec. trav. chim., 61, 500-12 (1942)—C.A. 38, 3564.
47. H. J. Backer and J. Kramer, Rec. trav. chim., 52, 916-22 (1933); *ibid.*, 53, 1101-12 (1934)—C.A. 28, 464; 29, 1061.
48. H. J. Backer and P. L. Stedehouder, Rec. trav. chim., 52, 923-34, 1039-45 (1933)—C.A. 28, 4040, 4714.
49. H. J. Backer and F. Stienstra, (a) Rec. trav. chim., 51, 1197-9 (1932); *ibid.*, 52, 912-5 (1933); *ibid.*, 54, 38-46, 607-17 (1935); (b) *ibid.*, 52, 1033-8 (1933); 54, 607-17 (1935)—C.A. 27, 1455; 28, 464; 29, 2507; 30, 3773; 28, 4713; 30, 3773.
50. H. J. Backer and E. Westerhuis, (a) Rec. trav. chim., 71, 1065-70 (1952); (b) *ibid.*, 1071-81; (c) *ibid.*, 1082-5—C.A. 47, 9898.
51. W. E. Bacon and W. M. LeSuer, J. Am. Chem. Soc., 76, 670-6 (1954)—C.A. 49, 2998.
52. D. E. Badertscher, F. M. Seger, and H. G. Berger, U.S. pat. 2,319,183 (1943)—C.A. 37, 6449.
53. Badische Anilin- & Soda-Fabrik, Ger. pat. 840,693 (1952)—C.A. 47, 1727.

54. R. H. Baker and Charles Barkenbus, *J. Am. Chem. Soc.*, **58**, 262-4 (1936)—C.A. **30**, 2961.
55. R. H. Baker, R. M. Dodson, and B. Riegel, *J. Am. Chem. Soc.*, **68**, 2636-9 (1946)—C.A. **41**, 2057.
56. H. J. Ball and T. C. Allen, *J. Econ. Entomol.*, **42**, 394-6 (1949)—C.A. **44**, 270.
57. L. L. Bambas, *J. Am. Chem. Soc.*, **67**, 668-70, 671-3 (1945)—C.A. **39**, 2493, 2494.
58. J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Am. Chem. Soc.*, **76**, 4348-67 (1954)—C.A. **49**, 11098.
59. M. M. Barnes, G. E. Carman, W. H. Ewart, and F. A. Gunther, *Advances in Chem. Ser., No. 1*, 112-6 (1950)—C.A. **44**, 7008.
60. George Barsky and R. V. Heuser to Am. Cyanamid Co., U.S. pat. 1,889,943 (1932)—C.A. **27**, 1721.
61. J. H. Bartlett, H. W. Rudel, and E. B. Cyphers to S. O. Dev. Co., U.S. pat. 2,611,728, 2,611,729 (1952)—C.A. **47**, 2930.
62. P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 405-7 (1950)—C.A. **45**, 1022.
63. M. Battegay and W. Kern, *Bull. soc. chim.*, [4] **41**, 34-47 (1927)—C.A. **21**, 1626.
64. Paul Baumgarten, (a) *Ber.*, **63**, 1330-5 (1930); (b) *Ger. pat.* 530,733 (1930)—C.A. **24**, 4281; **26**, 152.
65. R. L. Beard, *J. Econ. Entomol.*, **42**, 293-300 (1949)—C.A. **43**, 9340.
66. E. O. Beckmann, *J. prakt. Chem.*, [2] **17**, 456 (1878).
67. M. H. Bedford, R. J. Austin, and W. L. Webb, *J. Am. Chem. Soc.*, **57**, 1408-11 (1935)—C.A. **29**, 6491.
68. M. H. Bedford, R. B. Mason, and C. E. Morrell, *J. Am. Chem. Soc.*, **56**, 280-3 (1934)—C.A. **28**, 1916.
69. Otto Behagel and K. Hofmann, *Ber.*, **72**, 582-93, 697-712 (1939)—C.A. **33**, 4240, 4970.
70. Otto Behagel and Wilhelm Miller, *Ber.*, **67**, 105-8 (1934); *ibid.*, **68**, 1540-9 (1935)—C.A. **28**, 2001; **29**, 7303.
71. Otto Behagel and H. Seibert, *Ber.*, **65**, 812-6 (1932); *ibid.*, **66**, 708-17 (1933)—C.A. **26**, 4800; **27**, 4785.
72. E. Bekier, *Roczniki Chem.*, **16**, 64-7 (1936)—C.A. **30**, 5865.
73. E. Bekier and Z. Zelazna, *Roczniki Chem.*, **14**, 944-1003 (1934)—C.A. **29**, 6130.
74. Alan Bell and K. C. Brannock to Eastman Kodak Co., U.S. pat. 2,571,656 (1951)—C.A. **46**, 3065.

75. M. A. Belous and I. Ya. Postovskii, *J. Gen. Chem. USSR*, **20**, 1701-10 (1950)—C.A. **45**, 2391.
76. J. H. Billman, Joseph Garrison, R. Anderson, and Bernard Wolnak, *J. Am. Chem. Soc.*, **63**, 1920-1 (1941)—C.A. **35**, 5868.
77. J. H. Billman and E. O'Mahony, *J. Am. Chem. Soc.*, **61**, 2340 (1939)—C.A. **33**, 8587.
78. A. Binz, *Ber.*, **37**, 3549-50 (1904).
79. W. E. Blawvett and J. R. Hoffman, *N. Y. State Flower Growers Bull. No. 29*, 1-6 (1948)—C.A. **42**, 2720.
80. M. L. Bobb, (a) *J. Econ. Entomol.*, **42**, 343-5 (1949); (b) *ibid.*, **43**, 157-60 (1950)—C.A. **43**, 8088; **44**, 6074.
81. Bobingen Aktiengesellschaft für Textil-Faser (Paul Schlack), *Ger. pat.* 869,066 (1953)—C.A. **48**, 11485.
82. Horst Böhme and Erich Schneider, *Ber.*, **76**, 483-6 (1943)—C.A. **37**, 6575.
83. L. Bonnemaison, *Compt. rend. agr. France*, **33**, 554-6 (1947)—C.A. **42**, 3523.
84. H. S. Booth, D. R. Martin, and F. E. Kendall, *J. Am. Chem. Soc.*, **70**, 2523-5 (1948)—C.A. **43**, 1313.
85. C. V. Bowen and F. I. Edwards, Jr., *Advances in Chem. Ser., No. 1*, 198-201 (1950); *Anal. Chem.*, **22**, 706-8 (1950)—C.A. **44**, 7010.
86. K. C. Brannock, *J. Am. Chem. Soc.*, **73**, 4953-4 (1951)—C.A. **46**, 11100.
87. K. C. Brannock to Eastman Kodak Co., *U.S. pat.* 2,622,095 (1952)—C.A. **47**, 9343.
88. L. W. Brannon, *J. Econ. Entomol.*, **42**, 928-30 (1949)—C.A. **44**, 3659.
89. H. Bretschneider, *Oesterr. Akad. Wiss., Math.-naturw. Kl. Sitzber. Abt. IIb*, **159**, 372-84 (1950)—C.A. **47**, 6860.
90. H. Bretschneider and W. Klötzer, *Monatsh.*, **81**, 589-97 (1950)—C.A. **45**, 578.
91. C. H. Brett and W. C. Rhoades, *J. Econ. Entomol.*, **41**, 16-8 (1948)—C.A. **42**, 4708.
92. H. J. Bridger and R. W. Pittman, *J. Chem. Soc.*, **1950**, 1371-5—C.A. **45**, 115.
93. Herbert Brintzinger, *Ger. pat.* 848,951 (1952)—C.A. **47**, 6974.
94. Herbert Brintzinger and Hanz Ellwanger, *Ber.*, **87**, 300-14 (1954)—C.A. **49**, 4952.
95. Herbert Brintzinger, Hans Ellwanger, and Hermann Schmahl, *Angew. Chem.*, **64**, 398 (1952)—C.A. **47**, 7433.

96. Herbert Brintzinger, Hubert Koddebusch, E. E. Kling, and Gerhard Jung, *Ber.*, **85**, 455-7 (1952)—C.A. **47**, 1579.
97. Herbert Brintzinger and Malte Langheck, *Ber.*, **86**, 557-63 (1953), **87**, 325-30 (1954)—C.A. **49**, 4545.
98. Herbert Brintzinger, Malte Langheck, and Hans Ellwanger, *Ber.*, **87**, 320-4 (1954)—C.A. **49**, 4544.
99. Herbert Brintzinger, Malte Langheck, Hermann Schmahl, and Hans Ellwanger, *Angew. Chem.*, **64**, 398 (1952)—C.A. **47**, 7433.
100. Herbert Brintzinger, Karl Pfannstiel, Hubert Koddebusch, and K. E. Kling, *Ber.*, **83**, 87-90 (1950)—C.A. **44**, 5308.
101. Herbert Brintzinger and Hermann Schmahl, *Ber.*, **87**, 314-20 (1954)—C.A. **49**, 4544.
102. Herbert Brintzinger, Hermann Schmahl, and Hermann Witte, *Ber.*, **85**, 338-43 (1952)—C.A. **47**, 1694.
103. H. V. A. Briscoe, J. B. Peel, and P. L. Robinson, *J. Chem. Soc.*, 1929, 1048-50—C.A. **23**, 5126.
104. Walter Broeker, *J. prakt. Chem.*, [2] **118**, 287-94 (1928)—C.A. **22**, 1964.
105. T. E. Bronson, J. E. Dudley, Jr., and R. K. Chapman, *J. Econ. Entomol.*, **42**, 661-3 (1949)—C.A. **44**, 1217.
106. J. W. Brooks to Socony-Vac. Oil Co., U.S. pat. 2,571,332 (1951)—C.A. **47**, 148.
107. J. W. Brooks, E. G. Howard, and J. J. Wehrle, *J. Am. Chem. Soc.*, **72**, 1289-91 (1950)—C.A. **44**, 6410.
108. L. G. S. Brooks and Samuel Smiles, *J. Chem. Soc.*, 1926, 1723-9—C.A. **20**, 3289.
109. K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, **73**, 5787-9 (1951)—C.A. **47**, 480.
110. P. Bruin, A. F. Bickel, and E. C. Kooyman, *Rec. trav. chim.*, **71**, 1115-23 (1952)—C.A. **47**, 9908.
111. G. H. Buchanan to Am. Cyanamid Co., U.S. pat. 1,868,192 (1932)—C.A. **26**, 5105.
112. A. C. Buck, J. D. Bartleson, and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 744-6 (1948)—C.A. **42**, 4966.
113. A. C. Buck and H. P. Lankelma, *J. Am. Chem. Soc.*, **70**, 2396-7, 2398-2400 (1948)—C.A. **43**, 3353.
114. C. M. Buess and Norman Kharasch, *J. Am. Chem. Soc.*, **72**, 3520-32 (1950)—C.A. **45**, 1057.
115. Hans Bunte, *Ber.*, **7**, 646-8 (1874).
116. A. I. Busev, *Doklady Akad. Nauk SSSR*, **66**, 1093-6 (1949)—C.A. **43**, 7859.
117. F. D. Butcher, D. A. Wilbur, and P. A. Dahm, *J. Kansas Entomol. Soc.*, **23**, 22-6 (1950)—C.A. **44**, 5056.

118. G. D. Butler, Jr., and L. A. Carruth, *J. Econ. Entomol.*, **42**, 457-61 (1949)—C.A. **44**, 789.
119. J. C. Cage, *Analyst*, **75**, 189-91 (1950)—C.A. **44**, 7013.
120. A. Cahours and A. W. Hofmann, *Ann.*, **104**, 1-39 (1857).
121. Livio Cambi, *Chimica e industria* (Italy), **26**, 97-101 (1944)—C.A. **40**, 3734.
122. T. L. Cantrell and J. O. Turner to Gulf Oil Corp., U.S. pat. 2,169,634 (1939); 2,226,334 (1940)—C.A. **33**, 9624; **35**, 3076.
123. L. Carius, (a) *Ann.*, **112**, 190-201 (1859); (b) *ibid.*, **119**, 289-30 (1861).
124. F. W. Carlson and E. J. Newcomer, *J. Econ. Entomol.*, **42**, 338-42 (1949)—C.A. **43**, 9348.
125. C. E. Carman, W. H. Ewart, M. M. Barnes, and F. A. Gunther, *Advances in Chem. Ser., No. 1*, 128-36 (1950)—C.A. **44**, 7008.
126. E. L. Carr to Firestone Tire and Rubber Co., U.S. pat. 2,339,553, 2,354,427 (1944)—C.A. **38**, 4150; **39**, 3006.
127. G. Carrara, *Gaz. chim. ital.*, **23**, II, 12-7 (1893); *Atti Lincei*, **1893**, I, 421-5—*Ber.* **26R**, 605 (1893).
128. L. A. Carruth and W. L. Howe, *J. Econ. Entomol.*, **41**, 352-5 (1948)—C.A. **42**, 9049.
129. J. T. Cassaday to Am. Cyanamid Co., U.S. pat. 2,578,652 (1951); *Brit. pat.* 699,522 (1953)—C.A. **46**, 6139; **48**, 3992.
130. J. T. Cassaday, J. H. Fletcher, J. C. Hamilton, Ingenium Hechenbleikner, E. I. Hoegberg, B. J. Sertl, and J. T. Thurston, *Advances in Chem. Ser., No. 1*, 143-9 (1950)—C.A. **44**, 7009.
131. Leopold Cassella & Co., *Ger. pat.* 242,029 (1911); 247,416 (1912)—*C.* **1912**, I, 304; II, 169.
132. C. J. Cavallito and J. H. Bailey, *J. Am. Chem. Soc.*, **66**, 1950-1 (1944)—C.A. **39**, 323.
133. C. J. Cavallito, J. S. Buck, and C. M. Suter, *J. Am. Chem. Soc.*, **66**, 1952-4 (1944)—C.A. **39**, 324.
134. C. J. Cavallito and La V. D. Small to Sterling Drug Inc., U.S. pat. 2,508,745 (1950)—C.A. **44**, 9977.
135. F. S. Chamberlin, *J. Econ. Entomol.*, **42**, 544 (1949)—C.A. **44**, 266.
136. S. C. Chandler, *J. Econ. Entomol.*, **43**, 73-5 (1950)—C.A. **44**, 6074.
137. N. B. Chapman and B. C. Saunders, *J. Chem. Soc.*, **1948**, 1010-4—C.A. **43**, 121.

138. Chevrier, (a) *Compt. rend.*, 66, 748 (1868)—*Jahresb.*, 1868, 191, 734; (b) *Compt. rend.*, 68, 924 (1869); *Z. f. Chemie*, 1869, 413.
139. R. Child and Samuel Smiles, *J. Chem. Soc.*, 1926, 2696–702—*C.A.* 21, 234.
140. L. J. Christman to Am. Cyanamid Co., U.S. pat. 1,893,018 (1933)—*C.A.* 27, 2124.
141. J. W. Churchill to Mathieson Chem. Co., U.S. pat. 2,666,081 (1954)—*C.A.* 48, 12789.
142. R. E. D. Clark, *J. Chem. Soc.*, 1932, 1826–30—*C.A.* 26, 4332.
143. J. O. Clayton, B. B. Farrington, and R. L. Humphreys to S. O. Co. of Calif., U.S. pat. 2,274,291 (1942)—*C.A.* 36, 4706.
144. Clayton Aniline Co., *Ger. pat.* 120,504 (1900)—*Frdl.*, 6, 88.
145. T. F. Cleary, Jr., to Plant Prods. Corp., U.S. pat. 2,506,344 (1950)—*C.A.* 44, 6882.
146. Erik Clemmensen to Monsanto Chem. Co., U.S. pat. 1,945,183, 1,982,903 (1934)—*C.A.* 28, 2365; 29, 534.
147. Cloez, *Compt. rend.*, 24, 388 (1847)—*Jahresb.*, 1847–8, 695.
148. G. H. Cloud to S. O. Dev. Co., U.S. pat. 2,261,227 (1941)—*C.A.* 36, 1166.
149. Archibald Clow, H. M. Kirton, and J. M. C. Thompson, (a) *Trans. Faraday Soc.*, 36, 1028–38 (1940); (b) *ibid.*, 1029–33—*C.A.* 35, 1281.
150. J. H. Cochran, *J. Econ. Entomol.*, 42, 348–52 (1949)—*C.A.* 43, 7630.
151. Clyde Coleman to U.S. Rubber Co., U.S. pat. 2,010,059 (1935)—*C.A.* 29, 6471.
152. J. G. Conklin and G. L. Walker, *J. Econ. Entomol.*, 42, 153–4 (1949)—*C.A.* 43, 5897.
153. J. M. Connolly and G. M. Dyson, (a) *J. Chem. Soc.*, 1934, 822–4; (b) *ibid.*, 1935, 679–81; (c) *ibid.*, 1937, 827–8—*C.A.* 28, 5459; 29, 5086; 31, 5326.
154. E. W. Cook, P. H. Moss, and E. O. Hook to Am. Cyanamid Co., U.S. pat. 2,589,675 (1952)—*C.A.* 46, 11239.
155. E. W. Cook and W. D. Thomas, Jr., to Am. Cyanamid Co., (a) U.S. pat. 2,329,436 (1943); 2,344,394, 2,344,395, 2,361,746 (1944); 2,382,775 (1945); (b) 2,358,305 (1944); 2,373,811 (1945); (c) 2,365,938 (1944); 2,372,358 (1945)—*C.A.* 38, 1634, 3833, 3829; 39, 3153, 5472, 3925; 40, 1030; 39, 4751; 40, 1881.

156. W. S. Cook and R. A. Donia, *J. Am. Chem. Soc.*, **73**, 2275-7 (1951)—C.A. **46**, 925.
157. R. H. Cooper to Monsanto Chem. Co., U.S. pat. 2,339,002 (1944)—C.A. **38**, 4150.
158. R. T. Cotton, J. C. Frankenfeld, and N. M. Dennis, *Bur. Entomol. and Plant Quarantine*, *E-766*, 15 p. (1948)—C.A. **43**, 2361.
159. R. Coutin, *Parasitica (Gembloux)*, **5**, No. 2, 40-2 (1949)—C.A. **43**, 9388.
160. D. W. Cowie and D. T. Gibson, *J. Chem. Soc.*, 1933, 306-9—C.A. **27**, 2420.
161. J. A. Cox, (a) *J. Econ. Entomol.*, **42**, 507-14 (1949); (b) *ibid.*, 702-3; (c) *ibid.*, 632-5 (1949); *Penna. Agr. Exptl. Sta. Suppl. No. 3 to Bull. 502*, **2**, 10 (1949)—C.A. **44**, 790, 1221; **43**, 6777.
162. W. G. Craig to Lubri-Zol Corp., U.S. pat. 2,609,383 (1952)—C.A. **47**, 5443.
163. D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3883-9 (1949)—C.A. **44**, 10680.
164. G. S. Crandall, R. S. George, and E. M. Nygaard, to Socony-Vac. Oil Co., U.S. pat. 2,328,547, 2,328,709, 2,328,710, 2,328,711 (1943)—C.A. **38**, 1094, 1247.
165. J. T. Creighton and W. B. Gresham, *J. Econ. Entomol.*, **40**, 915-7 (1947)—C.A. **42**, 2710.
166. H. H. Crowell and H. E. Morrison, *J. Econ. Entomol.*, **43**, 14-6 (1950)—C.A. **44**, 5513.
167. O. D. Cunningham to P. C. Reilly, (a) U.S. pat. 1,813,346 (1931); (b) 1,902,838, 1,902,839 (1933)—C.A. **25**, 5131; **27**, 3183.
168. C. R. Cutright, *J. Econ. Entomol.*, **42**, 363-5 (1949)—C.A. **43**, 7630.
169. C. R. Cutright and T. H. Parks, *J. Econ. Entomol.*, **42**, 359-62 (1949)—C.A. **43**, 7629.
170. J. Cymerman and J. L. Lowe, *J. Chem. Soc.*, 1949, 1666—C.A. **44**, 600.
171. J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1951, 1332-7—C.A. **45**, 8354.
172. A. R. Davis to Am. Cyanamid Co., U.S. pat. 2,389,718 (1945); 2,409,344 (1946)—C.A. **40**, 1880; **41**, 1486.
173. E. G. Davis and Samuel Smiles, *J. Chem. Soc.*, **97**, 1290-9 (1910)—C.A. **4**, 3074.
174. L. L. Davis, B. H. Lincoln, and G. D. Byrkit to Continental Oil Co., U.S. pat. 2,278,719 (1942)—C.A. **36**, 6007.

175. I. M. Dawson, A. McL. Mathieson and J. M. Robertson, *J. Chem. Soc.*, 1948, 322-8—C.A. 42, 5740.
176. R. W. Dean, *J. Econ. Entomol.*, 43, 167-71 (1950)—C.A. 44, 6074.
177. Marcel Delépine, *Compt. rend.*, 154, 1171-3 (1912); *Bull. soc. chim.*, [4] 11, 576-81 (1912)—C.A. 6, 1749, 2421.
178. Marcel Delépine and J. Giron, *Bull. soc. chim.*, [4] 33, 1785-92 (1923)—C.A. 18, 1114.
179. Delmas and R. Coutin, *Compt. rend. acad. agr. France*, 34, 781-3 (1948)—C.A. 43, 3555.
180. W. S. Denham and Hilda Woodhouse, *J. Chem. Soc.*, 103, 1861-70 (1913)—C.A. 8, 905.
181. I. H. Derby to P. C. Reilly, U.S. pat. 1,729,097 (1929)—C.A. 23, 5151.
182. I. H. Derby and O. D. Cunningham to P. C. Reilly, (a) U.S. pat. 1,765,302 (1930); Reissue 18,116 (1931); (b) U.S. pat. 1,772,386 (1930); (c) 1,812,839 (1931)—C.A. 24, 3980; 25, 4839; 24, 4752; 25, 4839.
183. I. H. Derby and O. D. Cunningham to P. C. Reilly, (a) U.S. pat. 1,873,115 (1932); Reissue 19,192 (1934); (b) Can. pat. 310,001, 310,929 (1931)—C.A. 26, 5897; 28, 4691; 25, 2963.
184. L. Detroux, *Parasitica (Gembloux)*, 5, 68-82 (1949)—C.A. 44, 5058.
185. Deutsche Hydrierwerke, *Brit. pat.* 390,416 (1933)—C.A. 27, 4946.
186. J. B. Dickey and J. G. McNally to Eastman Kodak Co., (a) U.S. pat. 2,172,241 (1939); (b) 2,466,393 (1949)—C.A. 34, 1196; 43, 4877.
187. A. W. Dimock and C. H. Ford, *N. Y. State Flower Growers, Bull. No. 50*, 8 (1949)—C.A. 44, 2165.
188. T. N. Dobbins and W. D. Fronk, *J. Econ. Entomol.*, 41, 815-6 (1948)—C.A. 43, 1897.
189. C. B. Dominick, *J. Econ. Entomol.*, 42, 59-62 (1949)—C.A. 43, 5897.
190. Alfred Dornow, *Ber.*, 72, 568-70 (1939)—C.A. 33, 4213.
191. Kelvin Dorward, *Florida Entomologist*, 31, 116-22 (1948)—C.A. 43, 3139.
192. Gregg Dougherty and R. H. Barth to Heyden Chem. Corp., U.S. pat. 2,293,971 (1942)—C.A. 37, 889.
193. Gregg Dougherty and Otto Haas, *J. Am. Chem. Soc.*, 59, 2469-70 (1937)—C.A. 32, 518.
194. I. B. Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, 74, 5770-2 (1952)—C.A. 48, 8167.

195. I. B. Douglass and T. B. Johnson, *J. Am. Chem. Soc.*, **60**, 1486-9 (1938)—*C.A.* **32**, 5777.
196. I. B. Douglass and F. T. Martin, *J. Org. Chem.*, **15**, 795-9 (1950)—*C.A.* **45**, 1012.
197. I. B. Douglass, F. T. Martin, and Roger Addor, *J. Org. Chem.*, **16**, 1297-1302 (1951)—*C.A.* **46**, 2993.
198. I. B. Douglass and C. E. Osburne, *J. Am. Chem. Soc.*, **75**, 4582-3 (1953)—*C.A.* **48**, 6396.
199. I. B. Douglass, V. G. Simpson, and A. K. Sawyer, *J. Org. Chem.*, **14**, 272-6 (1949)—*C.A.* **43**, 6970.
200. Dow Chemical Co., *Brit. pat.* 671,142, 671,584, 673,877 (1952)—*C.A.* **46**, 10201; **47**, 3332.
201. F. B. Downing, A. F. Benning, and F. W. Johnson to Du Pont Co., *U.S. pat.* 2,263,618 (1941)—*C.A.* **36**, 1772.
202. L. R. Drake to Dow Chem. Co., *U.S. pat.* 2,552,536, 2,552,539 (1951); 2,615,039 (1952)—*C.A.* **46**, 136, 137; **47**, 9343.
203. L. R. Drake and A. J. Erbel to Dow Chem. Co., *U.S. pat.* 2,552,537, 2,552,540 (1951); *Brit. pat.* 684,734 (1952)—*C.A.* **46**, 136, 138; **47**, 4368.
204. L. R. Drake, E. E. Kenaga, and Arthur Erbel to Dow Chem. Co., *U.S. pat.* 2,552,541 (1951)—*C.A.* **46**, 138.
205. L. R. Drake and C. L. Moyle to Dow Chem. Co., *U.S. pat.* 2,552,538 (1951)—*C.A.* **46**, 136.
206. B. F. Driggers and M. M. Darley, *J. Econ. Entomol.*, **42**, 350-5 (1949)—*C.A.* **43**, 9348.
207. B. F. Driggers and L. G. Merrill, Jr., *J. Econ. Entomol.*, **42**, 351-4 (1949)—*C.A.* **43**, 7630.
208. K. P. DuBois, John Doull, P. R. Salerno, and J. M. Coon, *J. Pharmacol. Exptl. Therap.*, **95**, 79-91 (1949)—*C.A.* **43**, 3520.
209. Jules Duchesne, *Bull. soc. roy. sci. Liège*, **11**, 61-70 (1942)—*C.A.* **38**, 2567.
210. J. E. Dudley, Jr., T. E. Bronson, and P. V. Stone, *J. Econ. Entomol.*, **41**, 817 (1948)—*C.A.* **43**, 1897.
211. Phyllis M. Dunbar and L. P. Hammett, *J. Am. Chem. Soc.*, **72**, 109-12 (1950)—*C.A.* **44**, 4762.
212. E. I. du Pont de Nemours & Co., *Brit. pat.* 522,122, 522,123 (1940)—*C.A.* **36**, 1485, 1486.
213. G. M. Dyson, *Org. Syntheses*, Col. Vol. **1**, 493-497 (1932).
214. E. I. du Pont de Nemours & Co. and A. G. Jelinek, *Brit. pat.* 667,591 (1952)—*C.A.* **46**, 7122.
215. M. N. Dvornikoff and E. J. Young to Monsanto Chemical Co., *Brit. pat.* 684,839 (1952)—*C.A.* **48**, 1415.

216. G. M. Dyson and R. F. Hunter, *J. Soc. Chem. Ind.*, **45**, 81-5 T (1926)—C.A. **20**, 2313.
217. Sam Eagle and J. C. Warner, *J. Am. Chem. Soc.*, **58**, 2335-7 (1936)—C.A. **31**, 24.
218. W. H. Ebelke to U.S. Rubber Co., U.S. pat. 2,304,557 (1942)—C.A. **37**, 2746.
219. J. E. Eckert, *Am. Bee J.*, **88**, 129-31, 143-4 (1948); *J. Econ. Entomol.*, **41**, 487-91 (1948); **42**, 261-5 (1949)—C.A. **42**, 4708, 9052; **43**, 9349.
220. G. W. Eddy and W. S. McGregor, *J. Econ. Entomol.*, **42**, 547-8 (1949)—C.A. **44**, 788.
221. F. I. Edwards, Jr., *Anal. Chem.*, **21**, 1415-6 (1949)—C.A. **44**, 3201.
222. G. C. H. Ehrensvärd and Paul Brandt, *Arkiv Kemi, Mineral. Geol.*, **B21**, No. 4, 7 p. (1945)—C.A. **41**, 4115.
223. Hans Emde, Ger. pat. 804,572 (1951)—C.A. **46**, 530.
224. W. G. Emmett and H. O. Jones, *J. Chem. Soc.*, **99**, 713-20 (1911)—C.A. **5**, 3048.
225. E. F. Engelke to Cities Service Oil Co., U.S. pat. 2,403,792 (1946)—C.A. **40**, 6099.
226. Fritz Ephraim, Ber., **44**, 631-7 (1911)—C.A. **5**, 1783.
227. Etablissements Poulenc Frères and Carl Oechslin, Fr. pat. 643,911 (1927)—C.A. **23**, 1649.
228. E. A. Evans and J. S. Elliott, U.S. pat. 2,396,839 (1946); Brit. pat. 574,445 (1946)—C.A. **40**, 3894; **43**, 844.
229. W. L. Evers to Socony-Vacuum Oil Co., U.S. pat. 2,188,943 (1940)—C.A. **34**, 4560.
230. W. E. Ewart and G. E. Carman, *Citrus Leaves*, **29**, No. 3, 12-3, 38 (1949)—C.A. **43**, 4805.
231. Farbenfab. vorm. Fr. Bayer & Co., (a) Ger. pat. 32,829 (1885); (b) 46,333 (1888)—Ber., **18R**, 679 (1885); **22R**, 115 (1889).
232. Farbenfabriken Bayer, (a) Ger. pat. 830,508 (1952); Brit. pat. 691,374 (1953); (b) 670,030 (1952)—C.A. **47**, 4358, 8772, 5438.
233. Farbenfabriken Bayer (Walter Lorenz), (a) Ger. pat. 817,753 (1951); (b) 871,448 (1953)—C.A. **47**, 3879; **48**, 1414.
234. Farbenfabriken Bayer (Gerhard Schrader), (a) Ger. pat. 818,352 (1951); (b) 830,509 (1952); (c) 850,677 (1952)—C.A. **47**, 5959, 1727, 4034.
235. Farbenfabriken Bayer (Gerhard Schrader and Rudolf Muhlmann), Ger. pat. 848,812 (1952)—C.A. **47**, 5425.

236. Philip Fay and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 4933-5 (1952)—C.A. **47**, 12262.
237. Remo de Fazi, *Gazz. chim. ital.*, **53**, 175-6 (1923)—C.A. **17**, 2402.
238. Hans Feichtinger and Joseph Moos, *Ber.*, **81**, 371-5 (1948)—C.A. **43**, 4629.
239. L. C. Fife, R. L. Walker, and F. F. Bondy, *J. Econ. Entomol.*, **42**, 682-4 (1949)—C.A. **44**, 1219.
240. L. Filipczyk, *Roczniki Chem.*, **18**, 36-8 (Eng. 37-8), 117-9 (Eng. 119) (1938)—C.A. **32**, 4415; **33**, 29.
241. A. H. Fischer to Minerec Corp., (a) U.S. pat. 2,376,242 (1945); 2,434,357 (1948); (b) 2,574,554 (1951)—C.A. **39**, 3236; **42**, 3425; **46**, 9577.
242. J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, Beatrice J. Sertl, and J. T. Cassaday, (a) *J. Am. Chem. Soc.*, **70**, 3943-4 (1948); (b) *ibid.*, **72**, 2461-4 (1950)—C.A. **43**, 1313.
243. Ferdinand Flury and Franz Zernik, *Schädliche Gase, Dämpfe, Nebel, Rauch und Staubarten*, p. 362. Berlin, J. Springer.
244. A. Fock and K. Klüss, *Ber.*, **23**, 534-41 (1890).
245. F. Foerster and H. Umbach, *Z. anorg. allgem. Chem.*, **217**, 175-88 (1934)—C.A. **28**, 4673.
246. H. B. Footner and Samuel Smiles, *J. Chem. Soc.*, **127**, 2887-91 (1925)—C.A. **20**, 747.
247. N. E. Foss, Fitzgerald Dunning and G. L. Jenkins, *J. Am. Chem. Soc.*, **56**, 1978-80 (1934)—C.A. **28**, 6709.
248. N. E. Foss, J. J. Stehle, H. M. Shusett, and D. Hadburg, *J. Am. Chem. Soc.*, **60**, 2729-30 (1938)—C.A. **33**, 162.
249. Olav Foss, (a) *J. Am. Chem. Soc.*, **69**, 2236-7 (1947); (b) *Acta Chem. Scand.*, **1**, 307-27 (1947); (c) *ibid.*, 8-31; *Kgl. Norske Videnskab. Selskabs. Forh.*, **15**, 119-22 (1942); (d) *Acta Chem. Scand.*, **5**, 115-20 (1951); (e) *ibid.*, **6**, 306-7 (1952)—C.A. **42**, 142, 2240, 2537; **41**, 1599; **46**, 2481; **47**, 2725.
250. Olav Foss, Sven Furberg, and Eva Hadler, *Acta Chem. Scand.*, **5**, 1417-8 (1951)—C.A. **46**, 10770.
251. P. F. Frankland, Frederick Challenger and D. Webster, *J. Soc. Chem. Ind.*, **39**, 256-7 T (1920)—C.A. **14**, 3068.
252. H. C. Freuler to Union Oil Co. of Calif., U.S. pat. 2,364,283, 2,364,284 (1944)—C.A. **39**, 4475.
253. M. P. Frezal, *Compt. rend. acad. agr. France*, **35**, 463-7 (1949)—C.A. **44**, 5057.

254. C. Friedel and A. Ladenburg, *Ann. chim. phys.*, [4] 27, 416–28 (1872).
255. P. Friedländer and A. Simon, *Ber.*, 55, 3969–80 (1922)—*C.A.* 17, 2880.
256. A. H. Friend, *Agr. Gaz. N.S. Wales*, 60, 307–8, 334 (1949)—*C.A.* 44, 786.
257. K. Fries, *Ber.*, 45, 2965–73 (1912)—*C.A.* 7, 1006.
258. K. Fries with W. Buchler, *Ann.*, 454, 121–324 (1927)—*C.A.* 21, 2692.
259. K. Fries with K. Eishold and B. Vahlberg, *Ann.*, 454, 121–324 (1927)—*C.A.* 21, 2692.
260. K. Fries and G. Schürmann, (a) *Ber.*, 47, 1195–203 (1914); (b) *ibid.*, 52, 2170–81 (1919); (c) *ibid.*, 2182–95—*C.A.* 8, 2382; 14, 2182, 2183.
261. Emil Fromm, (a) *Ber.*, 41, 3397–425 (1908); (b) *Z. angew. Chem.*, 24, 1125 (1911); (c) *Ann.*, 396, 75–102 (1913)—*C.A.* 3, 154; 6, 1600; 7, 1710.
262. Emil Fromm and F. Erfurt, *Ber.*, 42, 3816–22 (1909)—*C.A.* 4, 212.
263. Emil Fromm and J. de S. Palma, (a) *Ber.*, 39, 3308–17 (1906); (b) *ibid.*, 3317–26—*C.A.* 1, 293, 145.
264. W. D. Fronk and T. N. Dobbins, U.S. Dept. Agr., Bur. Entomol. and Plant Quarantine, *E-782*, 10 p. (1949)—*C.A.* 43, 7182.
265. C. E. Funk, Jr., to Am. Cyanamid Co., U.S. pat. 2,466,408 (1949)—*C.A.* 43, 4845.
266. R. C. Fuson, D. M. Burness, R. E. Foster, and R. D. Lipscomb, *J. Org. Chem.*, 11, 499–503 (1946)—*C.A.* 41, 691.
267. R. C. Fuson, C. C. Price, R. A. Bauman, O. H. Bullitt, Jr., W. R. Hatchard, and E. W. Maynert, *J. Org. Chem.*, 11, 469–74 (1946)—*C.A.* 41, 687.
268. J. C. Gage, *Analyst*, 77, 123–6 (1952)—*C.A.* 46, 5247.
269. J. C. Gaines, *J. Econ. Entomol.*, 40, 896–9 (1948)—*C.A.* 42, 3898.
270. J. C. Gaines and H. A. Dean, (a) *J. Econ. Entomol.*, 41, 548–54 (1948); (b) *ibid.*, 808–9; (c) *ibid.*, 945–8; *ibid.*, 42, 956–9 (1949); (d) *ibid.*, 795–8—*C.A.* 43, 1142, 1897, 3135; 44, 3659, 1640.
271. M. L. Galashina, I. L. Vladimirova, Ya. A. Mandel'baum, and N. N. Mel'nikov, *Zhur. Obshehei Khim.*, 23, 533–5 (1953)—*C.A.* 48, 3887.
272. Kenneth Gardner and D. F. Heath, *Anal. Chem.*, 25, 1849–53 (1953)—*C.A.* 48, 2975.

273. Philip Garman, *J. Econ. Entomol.*, **43**, 53-6 (1950)—C.A. **44**, 6074.
274. B. G. Gavrilov and V. E. Tishenko, *Zhur. Obshehei Khim.*, **18**, 1687-91 (1948)—C.A. **43**, 2569.
275. J. W. Gaynor and C. M. Loane to S. O. Co. of Ind., U.S. pat. 2,362,624 (1944)—C.A. **39**, 5468.
276. Ronald Geballe and F. S. Linn, *J. Applied Phys.*, **21**, 592-4 (1950)—C.A. **44**, 8185.
277. Erich Gebauer-Fülneegg, *J. Am. Chem. Soc.*, **49**, 2270-5 (1927)—C.A. **21**, 3355.
278. Erich Gebauer-Fülneegg and H. A. Beatty, *J. Am. Chem. Soc.*, **49**, 1361-5 (1927)—C.A. **21**, 1971.
279. Erich Gebauer-Fülneegg and Eugen Riesz, *Monatsh.*, **47**, 57-61 (1926); **49**, 31-40 (1928)—C.A. **21**, 905; **22**, 3400.
280. Erich Gebauer-Fülneegg, Eugen Riesz, and F. Kessler, *Monatsh.*, **52**, 365-71 (1929)—C.A. **24**, 601.
281. Erich Gebauer-Fülneegg, Eugen Riesz, A. Lorenz, and R. Pollak, *Monatsh.*, **48**, 645-58 (1927)—C.A. **22**, 1148.
282. J. G. G. Gellatley, *Agr. Gas N.S. Wales*, **59**, 540-1 (1948)—C.A. **44**, 784.
283. R. S. George to Socony-Vac. Oil Co., U.S. pat. 2,307,624 (1943)—C.A. **37**, 3588.
284. R. S. George, G. S. Crandall, and E. M. Nygaard to Socony-Vac. Oil Co., U.S. pat. 2,325,391 (1943)—C.A. **38**, 469.
285. R. S. George, G. S. Crandall, E. M. Nygaard, and D. E. Badertscher to Socony-Vac. Oil Co., U.S. pat. 2,266,021 (1941)—C.A. **36**, 2392.
286. W. A. Gersdorff and R. H. Nelson, *J. Econ. Entomol.*, **41**, 333-4 (1948)—C.A. **42**, 7922.
287. J. J. Giammaria to Socony-Vac. Oil Co., (a) U.S. pat. 2,410,650 (1946); (b) 2,476,037 (1949)—C.A. **41**, 1424; **43**, 7224.
288. P. A. Giang, *J. Assoc. Offic. Agr. Chemists*, **36**, 384-7 (1953)—C.A. **47**, 12739.
289. D. T. Gibson, (a) *J. Chem. Soc.*, **1930**, 12-4; (b) *ibid.*, **1931**, 2637-44; *ibid.*, **1932**, 1819-26; *J. Am. Chem. Soc.*, **55**, 2611-2 (1933)—C.A. **24**, 1843; **26**, 695, 4312; **27**, 3444.
290. D. T. Gibson and J. D. Loudon, *J. Chem. Soc.*, **1936**, 487-9—C.A. **31**, 3900.
291. D. T. Gibson, C. J. Miller, and Samuel Smiles, *J. Chem. Soc.*, **127**, 1821-4 (1925)—C.A. **19**, 3259.
292. Henry Gilman, Jack Robinson, and N. J. Beaber, *J. Am. Chem. Soc.*, **48**, 2715-8 (1926)—C.A. **20**, 3693.

293. Henry Gilman, L. E. Smith, and H. H. Parker, *J. Am. Chem. Soc.*, **47**, 851-60 (1925)—C.A. **19**, 1256.
294. J. M. Ginsburg, *J. Econ. Entomol.*, **41**, 649-50 (1948); *Proc. N. J. Mosquito Exter. Assoc.*, 35th Ann. Meeting, 28-35 (1948)—C.A. **43**, 1519, 9345.
295. J. M. Ginsburg, R. S. Filmer, and J. P. Reed, *J. Econ. Entomol.*, **43**, 90-4 (1950)—C.A. **44**, 6564.
296. J. M. Ginsburg, R. S. Filmer, J. P. Reed, and A. R. Paterson, *J. Econ. Entomol.*, **42**, 602-11 (1949)—C.A. **44**, 1216.
297. C. M. Gjullin, *J. Econ. Entomol.*, **42**, 984-5 (1949)—C.A. **44**, 4625.
298. E. H. Glass, *J. Econ. Entomol.*, **43**, 146-51 (1950)—C.A. **44**, 6075.
299. E. H. Glass and P. J. Chapman, *J. Econ. Entomol.*, **42**, 29-35 (1949)—C.A. **43**, 5527.
300. Margot Goehring, *Ber.*, **80**, 219-25 (1947)—C.A. **42**, 6749.
301. M. C. Goldsworthy and R. A. Wilson, *Plant Disease Reptr.*, **32**, 388-90 (1948)—C.A. **42**, 9053.
302. L. D. Goodhue and W. M. Florence to Phillips Petroleum Co., U.S. pat. 2,598,989 (1952)—C.A. **46**, 10524.
303. L. D. Goodhue and Carolyn E. Tissol to Phillips Petroleum Co., U.S. pat. 2,621,143 (1952)—C.A. **47**, 2928.
304. R. C. Gore, *Discussions Faraday Soc.*, 1950, No. 9, 138-43—C.A. **46**, 3408.
305. H. B. Gottlieb, *J. Am. Chem. Soc.*, **54**, 748-50 (1932)—C.A. **26**, 1590.
306. J. Goubeau and H. W. Wittmeier, *Z. anorg. u. allgem. Chem.*, **270**, 16-32 (1952)—C.A. **47**, 1519.
307. Edwin Gould and E. O. Hamstead, *J. Econ. Entomol.*, **41**, 887-90 (1948)—C.A. **43**, 2729.
308. G. E. Gould, *Soap, Sanit. Chemicals*, **24**, No. 3, 147, 149, 177, 179 (1948)—C.A. **44**, 5513.
309. Castillo Graham, *J. Econ. Entomol.*, **42**, 354-6 (1949)—C.A. **43**, 7628.
310. S. H. Greenbaum, *J. Am. Chem. Soc.*, **76**, 6052-4 (1954).
311. D. E. Greenwood and R. N. Hofmaster, *J. Econ. Entomol.*, **42**, 675-7 (1949)—C.A. **44**, 1218.
312. J. T. Griffiths, Jr., and J. R. King, *J. Econ. Entomol.*, **41**, 389-92 (1948)—C.A. **42**, 9049.
313. J. T. Griffiths, Jr., J. R. King, and W. L. Thompson, *Citrus Ind.*, **29**, No. 4, 11-4, 26 (1948)—C.A. **42**, 6980.
314. F. Guichard, *Ber.*, **32**, 1572-81 (1899).
315. F. A. Gunther, M. M. Barnes, and G. E. Carman, *Advances in Chem. Ser.*, No. 1, 137-42 (1950)—C.A. **44**, 7009.

316. F. A. Gunther and R. C. Blinn, *Advances in Chem. Ser., No. 1*, 72-87 (1950)—C.A. 44, 7006.
317. A. Gutmann, (a) *Ber.*, 40, 2818-22 (1907); (b) *ibid.*, 41, 1650-5 (1908); (c) *ibid.*, 3351-6; *ibid.*, 42, 228-32 (1909); (d) *ibid.*, 47, 635-9 (1914)—C.A. 1, 2556; 2, 2374; 3, 175, 894; 8, 1587.
318. A. Gutmann, (a) *Ber.*, 48, 1162-6 (1915); (b) *ibid.*, 49, 949-54 (1916); (c) *Z. anal. Chem.*, 71, 43-5 (1927)—C.A. 9, 2744; 10, 2669; 21, 2659.
319. G. G. Gyrisco, L. D. Newsom, D. S. Marshall, and H. H. Schwardt, *J. Econ. Entomol.*, 42, 311-4 (1949)—C.A. 43, 8599.
320. E. Häffliger, *J. Econ. Entomol.*, 42, 523-8 (1949)—C.A. 44, 789.
321. J. Hagen and W. Reinl, *Munch. med. Wochschr.*, 92, 449-59 (1950)—C.A. 47, 7723.
322. S. A. Hall, *Advances in Chem. Ser., No. 1*, 150-9 (1949)—C.A. 44, 7009.
323. D. W. Hamilton, *J. Econ. Entomol.*, 41, 244-8 (1948)—C.A. 42, 7922.
324. M. S. Hansen to P. C. Reilly, U.S. pat. 1,972,588 (1934)—C.A. 28, 6417.
325. R. S. Hanslick to U.S. Rubber Co., U.S. pat. 2,304,568 (1942)—C.A. 37, 6159.
326. A. Hantzsch, *Ann.*, 296, 84-94 (1897).
327. M. W. Harman to Monsanto Chem. Co., U.S. pat. 2,191,657 (1940)—C.A. 34, 4610.
328. S. W. Harman, *J. Econ. Entomol.*, 41, 210-2 (1948); N. Y. Agr. Exptl. Sta., *Bull. No. 733*, 3-23 (1948)—C.A. 42, 7919; 43, 9347.
329. J. F. Harris, Jr., *Univ. Microfilms (Ann Arbor, Mich.)*, *Pub. No. 4927*, 111 p.; *Dissertation Abstr.*, 13, 177 (1953)—C.A. 48, 2636.
330. P. K. Harrison, *Bur. Entomol. and Plant Quarantine, E-770*, 5 p. (1949)—C.A. 43, 7183.
331. L. E. Hart, E. W. McClelland, and F. S. Fowkes, *J. Chem. Soc.*, 1938, 2114-7—C.A. 33, 1726.
332. Albert Hartzell, *Advances in Chem. Ser., No. 1*, 99-101 (1950)—C.A. 44, 7007.
333. R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 1953, 3219-25—C.A. 48, 12668.
334. W. B. Hathaway, N. Y. State Flower Growers, *Bull. No. 50*, 3 (1949)—C.A. 44, 2166.

335. Heinz Haury, Seifen-Oele-Fette, Wachse, 75, 463-4 (1949)—C.A. 44, 1215.
336. J. H. Hawkins and Richard Thurston, J. Econ. Entomol., 42, 306-11 (1949)—C.A. 43, 6354.
337. N. C. Hayslip, Florida Entomologist, 31, 80-7 (1948)—C.A. 43, 7628.
338. L. W. Hazleton and Emily G. Holland, Advances in Chem. Ser., No. 1, 31-8 (1950)—C.A. 44, 7005.
339. Ingenuin Hechenbleikner to Am. Cyanamid Co., U.S. pat. 2,482,063 (1949); Brit. pat. 653,603 (1951)—C.A. 44, 4022; 45, 8547.
340. R. E. Hein and R. H. McFarland, J. Am. Chem. Soc., 74, 1856-7 (1952)—C.A. 48, 1246.
341. O. B. Helfrich and E. E. Reid, J. Am. Chem. Soc., 43, 591-4 (1921)—C.A. 15, 1551.
342. Henkel & Cie, (a) Brit. pat. 397,445 (1933); (b) Fr. pat. 765,360 (1934); Brit. pat. 417,930 (1934); (c) Fr. pat. 788,606 (1935); Brit. pat. 439,177 (1935); (d) Ger. pat. 619,299 (1935)—C.A. 28, 924, 6958; 29, 1433; 30, 1394, 3132, 1386.
343. Henkel & Cie (W. J. Kaiser and Alfred Kirstahler), Ger. pat. 639,281 (1936)—C.A. 31, 1524.
344. Henkel & Cie (Alfred Kirstahler and W. J. Kaiser), Ger. pat. 636,260 (1936)—C.A. 31, 701.
345. G. A. Hepburn, Citrus Grower (S. Africa), No. 179, 2-5 (1948)—C.A. 44, 4625.
346. R. W. Hess and J. M. Leaper to Barrett Co., (a) U.S. pat. 1,729,615 (1929); (b) 1,904,462 (1933)—C.A. 23, 5474; 27, 3436.
347. L. A. Hetrick, J. Econ. Entomol., 43, 57-9 (1950)—C.A. 44, 6075.
348. T. P. Hilditch, J. Chem. Soc., 97, 1091-8 (1910)—C.A. 4, 2937.
349. C. M. Himel and L. O. Edmonds to Phillips Pet. Co., (a) U.S. pat. 2,520,400, 2,520,401 (1950); (b) 2,572,564, 2,572,565, 2,572,567 (1951); (c) 2,572,845 (1951); (d) 2,574,829 (1951)—C.A. 44, 10735; 46, 6149, 9589, 4565.
350. O. Hinsberg, (a) Ber., 36, 107-15 (1903); (b) *ibid.*, 41, 2836-9 (1908); (c) *ibid.*, 4294-7—C.A. 2, 3361; 3, 650.
351. E. I. Hoegberg to Am. Cyanamid Co., (a) U.S. pat. 2,494,126 (1950); Ger. pat. 807,687 (1951); (b) U.S. pat. 2,632,020 (1953)—C.A. 44, 3515; 46, 7582; 48, 2759.

352. E. I. Hoegberg and J. T. Cassaday, *J. Am. Chem. Soc.*, **73**, 557-9 (1951)—*C.A.* **45**, 5609.
353. J. R. Hoffman, *N. Y. State Flower Growers, Bull. No. 51*, 7-8 (1949)—*C.A.* **44**, 3664.
354. R. A. Hoffman and A. W. Lindquist, *J. Econ. Entomol.*, **42**, 436-8 (1949)—*C.A.* **44**, 271.
355. A. W. Hofmann and F. Mahla, *Ber.*, **25**, 2436-44 (1892).
356. R. N. Hofmaster and D. E. Greenwood, *J. Econ. Entomol.*, **42**, 502-6 (1949)—*C.A.* **44**, 789.
357. T. W. Hogan and D. S. Morris, *J. Dept. Agr. Victoria*, **47**, 260-4 (1949)—*C.A.* **44**, 786.
358. E. R. Holiday, J. St. L. Philpot, and L. A. Stocken, *Biochem. J.*, **47**, 637-9 (1950)—*C.A.* **45**, 8468.
359. E. O. Hook and L. C. Beegle to American Cyanamid Co., U.S. pat. 2,627,523 (1953)—*C.A.* **47**, 5110.
360. E. O. Hook and P. H. Moss to American Cyanamid Co., U.S. pat. 2,565,920, 2,565,921, 2,566,129 (1951); 2,586,655, 2,596,076, 2,614,988 (1952); *Brit. pat.* 676,776 (1952)—*C.A.* **46**, 3067; **47**, 4358; **46**, 8144, 8322; **47**, 4079, 9995.
361. H. T. Hookway, (a) *J. Am. Chem. Soc.*, **71**, 3240-1 (1949); (b) *J. Chem. Soc.*, 1950, 1932-4—*C.A.* **44**, 1050; **45**, 1057.
362. W. S. Hough, (a) *J. Econ. Entomol.*, **41**, 207-9 (1948); (b) *ibid.*, 983-4—*C.A.* **42**, 7921; **43**, 3139.
363. D. D. Howat, *Chem. Age (London)*, **42**, 343-5 (1940).
364. L. H. Howland to U.S. Rubber Co., U.S. pat. 2,382,793 (1945)—*C.A.* **40**, 368.
365. M. H. Hubacker, *Org. Syntheses, Col. Vol. II*, 455 (1943).
366. H. C. Hockett, *J. Econ. Entomol.*, **41**, 202-6 (1948)—*C.A.* **42**, 7921.
367. C. M. Hull to S. O. Co. of Ind., U.S. pat. 2,351,763 (1944)—*C.A.* **38**, 5225.
368. R. L. Humphries to S. O. Co. of Calif., U.S. pat. 2,157,452 (1939)—*C.A.* **33**, 6586.
369. Madison Hunt to DuPont Co., U.S. pat. 2,390,713 (1945)—*C.A.* **40**, 1875.
370. A. M. Hutchison and Samuel Smiles, *J. Chem. Soc.*, **101**, 570-6 (1912)—*C.A.* **6**, 3263.
371. I. G. Farben., (a) *Ger. pat.* 523,219 (1929); *Brit. pat.* 341,366 (1931); (b) *Ger. pat.* 612,665 (1935); (c) *Belg. pat.* 451,249 (1943)—*C.A.* **25**, 3429; **29**, 6327; **42**, 586.
372. I. G. Farben. (Eduard Tschunkur and Hugo Köhler), *Ger. pat.* 615,580 (1935)—*C.A.* **29**, 8408.

373. I. G. Farben. (Ewald Zaucker), Ger. pat. 586,351 (1933)—C.A. 28, 687.
374. William Iglinsky, Jr., and J. C. Gaines, J. Econ. Entomol., 42, 703-5 (1949)—C.A. 44, 1219.
375. Z. V. Ivanova, *Gigiena i Sanit.*, 1953, No. 4, 29-34—C.A. 47, 11646.
- 375.5. D. J. G. Ives, R. W. Pittman, and W. Wardlaw, J. Chem. Soc., 1947, 1080-3—C.A. 42, 834.
376. Michimasa Izumi and Makoto Yokoo to Yoshitomi Drug Mfg. Co., Japan pat. 2668 (1952)—C.A. 48, 2118.
377. Giovanni Jacini, *Chimica e industria* (Milan), 29, 244-5 (1947)—C.A. 42, 5843.
378. J. W. James, J. prakt. Chem., [2] 30, 316-7 (1885); *ibid.*, 35, 459-64 (1887); J. Chem. Soc., 51, 268-74 (1887).
379. D. W. Jayne, Jr., to Am. Cyanamid Co., U.S. pat. 2,206,284 (1940); Brit. pat. 544,060, 546,232 (1942)—C.A. 34, 7276; 36, 6171; 37, 2966.
380. A. G. Jelinek to Du Pont Co., U.S. pat. 2,503,390 (1950)—C.A. 44, 6435.
381. W. Jenny, (a) *Helv. chim. acta*, 35, 845-51, 1429-34, 1591-4 (1952); (b) *ibid.*, 36, 1278-82 (1953)—C.A. 47, 4322; 48, 10709.
382. J. A. Jensen and G. W. Pearce, J. Am. Chem. Soc., 74, 3184 (1952)—C.A. 48, 3887.
383. Carl Johansen and E. P. Breakey, (a) J. Econ. Entomol., 42, 543 (1949); (b) *ibid.*, 562-3—C.A. 44, 787, 267.
384. B. L. Johnson, U.S. pat. 1,763,851, 1,763,852 (1930)—C.A. 24, 3746.
385. D. R. Johnson, J. Econ. Entomol., 42, 801-5 (1949)—C.A. 44, 2165.
386. G. A. Johnson, J. H. Fletcher, K. G. Nolan, and J. T. Cassaday, J. Econ. Entomol., 45, 279-83 (1952)—C.A. 47, 2123.
387. T. B. Johnson to Sharpe and Dohme, Inc., U.S. pat. 2,350,900 (1944)—C.A. 38, 5226.
388. T. B. Johnson and E. H. Hemingway, (a) J. Am. Chem. Soc., 38, 1550-7 (1916); (b) *ibid.*, 1860-7—C.A. 10, 2229, 2733.
389. T. B. Johnson and M. L. Moore, *Science*, 81, 643-4 (1935)—C.A. 29, 6219.
390. T. B. Johnson and A. A. Ticknor, J. Am. Chem. Soc., 40, 636-46 (1918)—C.A. 12, 905.

391. A. R. Jones and J. O. Smith, Jr., to S. O. Dev. Co., U.S. pat. 2,627,511 (1953)—C.A. 47, 4599.
392. S. C. Jones and R. G. Rosenstiel, *J. Econ. Entomol.*, **41**, 118 (1948)—C.A. 42, 6049.
393. M. I. Kabachnik and T. A. Mastryukova, (a) *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1952**, 727-35; (b) *ibid.*, **1953**, 121-5; (c) *ibid.*, 163-76—C.A. 47, 9909; 48, 3244, 3243.
394. Akira Kamido, *Nôgaku (Sci. of Agr.)*, **2**, 452-7 (1948)—C.A. 44, 7013.
395. Jonas Kamlet to Mathieson Chem. Corp., U.S. pat. 2,664,442 (1953)—C.A. 48, 3384.
396. Mildred E. Kamner, Dissertation, Columbia Univ.—C.A. 29, 4254.
397. A. N. Kappanna, (a) *J. Indian Chem. Soc.*, **6**, 45-52 (1929); (b) *ibid.*, 419-30—C.A. 23, 2870, 5394.
398. A. N. Kappanna and H. W. Patwardhan, *J. Indian Chem. Soc.*, **9**, 379-82 (1932)—C.A. 27, 655.
399. J. V. Karabinos, R. A. Paulson, and W. H. Smith, *J. Research Natl. Bur. Standards*, **48**, 322-4 (1952)—C.A. 47, 5877.
400. August Kekulé, *Ann.*, **90**, 309-16 (1854).
401. C. D. Kelso to S. O. Co. of Ind., U.S. pat. 2,315,529 (1943)—C.A. 37, 5857.
402. C. D. Kelso and L. W. Mixon to S. O. Co. of Ind., (a) U.S. pat. 2,316,085 (1943); (b) 2,316,090 (1943)—C.A. 37, 5858.
403. B. A. Kent and Samuel Smiles, *J. Chem. Soc.*, **1934**, 422-8—C.A. 28, 4395.
404. Kern and Sandoz, *Mon. sci.*, [4], **1**, 1328 (1887); *Jahresb.*, **1887**, 2545.
405. J. A. A. Ketelaar and H. R. Gersman, *J. Am. Chem. Soc.*, **72**, 5777 (1950)—C.A. 45, 5653.
406. J. A. A. Ketelaar, H. R. Gersman, and K. Koopmans, *Rec. trav. chim.*, **71**, 1253-8 (1952)—C.A. 47, 8487.
407. Norman Kharasch, *J. Am. Chem. Soc.*, **72**, 3322-3 (1950)—C.A. 44, 10673.
408. Norman Kharasch and S. J. Assony, *J. Am. Chem. Soc.*, **75**, 1081-2 (1953)—C.A. 48, 2634.
409. Norman Kharasch and T. C. Bruice, *J. Am. Chem. Soc.*, **73**, 3240-4 (1951)—C.A. 46, 3023.
410. Norman Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724-8 (1949)—C.A. 44, 2467.

411. Norman Kharasch, C. M. Buess, and William King, *J. Am. Chem. Soc.*, **75**, 6035-8 (1953)—C.A. **49**, 1624.
412. Norman Kharasch, C. M. Buess, and S. I. Strashun, *J. Am. Chem. Soc.*, **74**, 3422-3 (1952)—C.A. **48**, 3292.
413. Norman Kharasch and J. L. Cameron, *J. Am. Chem. Soc.*, **73**, 3864-7 (1951); *ibid.*, **75**, 1077-81 (1953)—C.A. **46**, 1960; **48**, 2632.
414. Norman Kharasch, G. L. Gleason, and C. M. Buess, *J. Am. Chem. Soc.*, **72**, 1796-8 (1950)—C.A. **44**, 7258.
415. Norman Kharasch and A. J. Havlik, *J. Am. Chem. Soc.*, **75**, 3734-37 (1953)—C.A. **48**, 10650.
416. Norman Kharasch, D. P. McQuarrie, and C. M. Buess, *J. Am. Chem. Soc.*, **75**, 2658-60 (1953)—C.A. **48**, 7570.
417. Norman Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Reviews*, **39**, 269-332 (1946).
418. Norman Kharasch, H. L. Wehrmeister, and Henry Tigerman, *J. Am. Chem. Soc.*, **69**, 1612-5 (1947)—C.A. **41**, 6217.
419. H. L. King and Ray Hutson, *J. Econ. Entomol.*, **42**, 398-9 (1949)—C.A. **44**, 267.
420. H. L. King, Ray Hutson, and T. H. Farr, *J. Econ. Entomol.*, **41**, 976-7 (1948)—C.A. **43**, 2729.
421. W. V. King, *Am. J. Trop. Med.*, **28**, 487-97 (1948)—C.A. **43**, 9349.
422. Alfred Kirstahler and W. J. Kaiser, U.S. pat. 2,004,873 (1935)—C.A. **29**, 5124.
423. Árpád Kiss and Irén Bossányi, *Z. anorg. allgem. Chem.*, **224**, 33-9 (1935)—C.A. **29**, 7767.
424. Árpád Kiss, Irén Bossányi, and P. Vass, *Acta Lit. Sci. Univ. Hung. Francisco-Josephinae Sect. Chem. Mineral. Phys.*, **3**, 20-35 (1933)—C.A. **28**, 1915.
425. Árpád Kiss and P. Vass, *Z. anorg. allgem. Chem.*, **209**, 236-40 (1932); **217**, 305-20 (1934)—C.A. **27**, 1260; **28**, 3965.
426. A. R. Kittleson, *Anal. Chem.*, **24**, 1173-5 (1952); *Science*, **115**, 84-6 (1952)—C.A. **46**, 10052, 10134.
427. Kai Kjeldgaard, *Arch. Pharm. Chemi*, **57**, 187-92 (1950)—C.A. **44**, 5309.
428. H. A. Klasens, *Chem. Weekblad*, **38**, 448 (1941)—C.A. **36**, 6084.
429. H. A. Klasens and H. J. Backer, (a) *Rec. trav. chim.*, **58**, 941-7 (1939); (b) *ibid.*, **61**, 513-22 (1942)—C.A. **34**, 1303; **36**, 6862.

430. Peter Klason, (a) Lunds U-arsskrift, *XI*, 1875—Bull. soc. chim., [2] 25, 183–7 (1876); (b) J. prakt. Chem., [2] 15, 193–218 (1877); (c) Ber., 20, 2375–85 (1887); Ger. pat. 83,124—Ber., 28, R, 942 (1895).
431. Robert Klement and Albert May, Ber., 71, 890–4 (1938)—C.A. 32, 6640.
432. Robert Klement and Rudolf Reuber, Ber., 68, 1761–5 (1935)—C.A. 29, 7961.
433. H. Kloosterziel and H. J. Backer, Rec. trav. chim., 71, 373–8 (1952)—C.A. 46, 11194.
434. H. Kloosterziel, J. S. Boerema, and H. J. Backer, Rec. trav. chim., 72, 612–6 (1953)—C.A. 48, 8763.
435. August Knop, Ber., 20, 3352–3 (1888).
436. Hermann Kolbe, (a) Ann., 45, 41–6 (1843); (b) *ibid.*, 54, 145–88 (1845).
437. S. M. Kolthoff and W. E. Harris, Anal. Chem., 21, 963–5 (1949)—C.A. 44, 76.
438. Hermann Kopp, Ann., 35, 343–50 (1840).
439. G. M. Kosolapoff to Monsanto Chem. Co., (a) U.S. pat. 2,536,647 (1951); (b) 2,567,154 (1951); 2,582,204 (1952)—C.A. 45, 5185; 46, 2562, 7113.
440. A. Kovalevsky, Ann., 119, 303–13 (1861).
441. Serge Krapivin, J. chim. phys., 10, 289–305 (1912); Z. physik. Chem., 82, 439–47 (1913)—C.A. 7, 3887, 3888.
442. A. E. Kretov, A. W. Panchenko, and A. Konovalchik, J. Gen. Chem. (USSR), 1, 396–400 (1931)—C.A. 26, 2442.
443. W. M. Kulash, (a) J. Econ. Entomol., 41, 387–9 (1948); *ibid.*, 42, 558–9 (1949); (b) *ibid.*, 42, 677–80 (1949)—C.A. 42, 9051; 44, 785, 1219.
444. Frederick Kurzer, Nature, 170, 167–8 (1952); J. Chem. Soc., 1953, 549–56—C.A. 47, 10493; 48, 1991.
445. Frederick Kurzer and J. R. Powell, J. Chem. Soc., 1952, 3728–34—C.A. 47, 8031.
446. V. K. LaMer, (a) J. Am. Chem. Soc., 51, 3341–7 (1929); (b) J. Franklin Inst., 225, 709–37 (1938)—C.A. 24, 772; 32, 8889.
447. V. K. LaMer and R. W. Fessenden, J. Am. Chem. Soc., 54, 2351–66 (1932)—C.A. 26, 3719.
448. V. K. LaMer and Mildred E. Kamner, (a) Ind. Eng. Chem., 23, 878–81 (1931); (b) J. Am. Chem. Soc., 57, 2662–8, 2669–73 (1935)—C.A. 25, 5075; 30, 1643.
449. W. H. Lange, Jr., E. C. Carlson, and L. D. Leach, J. Econ. Entomol., 42, 942–55 (1949)—C.A. 44, 3659.

450. J. P. LaRocca and K. L. Waters, *J. Am. Pharm. Assoc.*, **39**, 521-3 (1950)—C.A. **44**, 11020.
451. E. Larsson and R. E. I. Marin to Uddeholms Aktiebolag, *Swed. pat.* 138,357 (1952)—C.A. **48**, 2761.
452. W. A. Lazier and P. L. Salzberg to DuPont Co., *U.S. pat.* 2,402,591 (1946)—C.A. **40**, 5769.
453. E. K. Learmouth and Samuel Smiles, *J. Chem. Soc.*, **1936**, 327-9—C.A. **30**, 3796.
454. H. Z. Lecher, (a) *Ber.*, **53**, 577-90, 591-3 (1920); (b) *ibid.*, **58**, 417-22 (1925)—C.A. **14**, 3079, 3080; **19**, 1855.
455. H. Z. Lecher and Elizabeth M. Hardy, *J. Org. Chem.*, **20**, 475-87 (1955)—C.A. **50**, 4101.
456. H. Z. Lecher and Fritz Holschneider, *Ber.*, **57**, 755-8 (1924)—C.A. **18**, 2877.
457. H. Z. Lecher, Fritz Holschneider, Karl Köberle, Walter Speer, and Paul Stöcklin, *Ber.*, **58**, 409-16 (1925)—C.A. **19**, 1855.
458. H. Z. Lecher, Karl Köberle, and Paul Stöcklin, *Ber.*, **58**, 423-4 (1925)—C.A. **19**, 1856.
459. H. Z. Lecher and Werner Siefken, *Ber.*, **59**, 1314-21, 2594-2601 (1926)—C.A. **20**, 2976; **21**, 890.
460. H. Z. Lecher and Kurt Simon, (a) *Ber.*, **54**, 632-8 (1921); (b) *ibid.*, 2249-51; **55**, 2423-32 (1922)—C.A. **15**, 2849; **16**, 181; **17**, 739.
461. H. Z. Lecher and Max Wittwer, *Ber.*, **55**, 1474-80 (1922)—C.A. **16**, 3887.
462. A. J. Lehman, *Assoc. Food and Drug Officials, U.S. Quart. Bull.*, **12**, 82-9 (1948); *ibid.*, **13**, 65-70 (1949)—C.A. **43**, 2705; **44**, 6071.
463. A. B. Lemmon, *Citrus Leaves*, **29**, No. 7, 6-7, 28 (1949)—C.A. **43**, 8600.
464. Felix Lengfeld, *Ber.*, **28**, 449-51 (1895).
465. A. R. Leonard, *Calif. Health*, **7**, 105-6 (1950)—C.A. **44**, 3202.
466. H. S. Lepage, O. Giannotti, and A. Orlando, (a) *Arquiv. inst. biol. (Sao Paulo)*, **18**, 1-30 (1947-48); (b) *ibid.*, 135-60—C.A. **43**, 4805, 4806.
467. A. W. Lewis and J. E. Schott to Tidewater Assoc. Oil Co., *U.S. pat.* 2,417,876 (1947)—C.A. **41**, 3958.
468. J. P. Linduska and E. W. Surber, *U.S. Dept. Interior, Fish and Wildlife Service, Circ.* **15**, 19 p. (1948)—C.A. **43**, 1523.

469. David Lipkin to Atlantic Refg. Co., (a) U.S. pat. 2,146,584 (1939); (b) 2,109,491 (1938); 2,192,921 (1940)—C.A. 33, 3581; 32, 3144; 34, 4836.
470. Arnold Lippert and E. E. Reid, J. Am. Chem. Soc., 60, 2370-1 (1938)—C.A. 33, 127.
- 470.5. E. Lippmann and I. Pollak, Ber., 34, 2767 (1901).
471. Chien-Pen Lo, H. F. Wilson and W. J. Croxall, J. Am. Chem. Soc., 76, 1704-5 (1954)—C.A. 49, 6165.
472. C. M. Loane and J. W. Gaynor to S. O. Co. of Ind., (a) U.S. pat. 2,315,088, 2,316,078, 2,316,080, 2,316,081 (1943); (b) 2,316,082 (1943); (c) 2,316,087 (1943)—C.A. 37, 5858, 5859.
473. C. M. Loane, J. W. Gaynor, and L. W. Mixon to S. O. Co. of Ind., U.S. pat. 2,316,083, 2,316,084 (1943)—C.A. 37, 5859.
474. Siegfried Lockau and Manfred Lüdicke, Z. Naturforsch., 7b, 389-97 (1952)—C.A. 47, 6366.
475. H. D. Loden and H. O. Lund, J. Econ. Entomol., 41, 851-3 (1948)—C.A. 43, 2729.
476. O. Loew, Zeit. f. Chem., V, 82-4 (1869).
477. Carl Löwig and Salomon Weidmann, Pogg. Ann., 49, 323-40 (1840).
478. F. A. Long and A. R. Olson, J. Phys. Chem., 41, 267-81 (1937)—C.A. 31, 4192.
479. Lukaschewicz, Z. f. Chemie, 1868, 641.
480. V. O. Lukashevich and M. M. Sergeeva, Zhur. Obshechi Khim., 19, 1493-1510 (1949)—C.A. 44, 3452.
481. M. W. McAfee to Dow Chem. Co., U.S. pat. 2,198,915 (1940)—C.A. 34, 5815.
482. E. W. McClelland and L. A. Warren, J. Chem. Soc., 1930, 2690-3—C.A. 25, 1228.
483. Hamilton McCombie, B. C. Saunders, N. B. Chapman, and Robert Heap, U.S. pat. 2,489,917 (1949)—C.A. 44, 3005.
484. Hamilton McCombie, B. C. Saunders, N. B. Chapman, Robert Heap, and J. D. Pratt, Brit. pat. 602,446 (1948)—C.A. 42, 8208.
485. J. P. McDermott to S. O. Dev. Co., U.S. pat. 2,631,132 (1953)—C.A. 47, 5111.
486. F. H. McLaren to S. O. Co. of Ind., U.S. pat. 2,316,086 (1943)—C.A. 37, 5858.
487. J. C. McNab and C. L. Fleming, Jr., to S. O. Dev. Co., U.S. pat. 2,420,893 (1947)—C.A. 41, 5298.

488. C. Märcker, *Ann.*, **136**, 75–95 (1865).
489. O. Y. Magidson and V. M. Kroll, *Trans. sci. chem. pharm. inst. (Moscow)*, **6**, 21–8 (1923)—C.A. **22**, 4077.
490. Lamberto Malatesta, (a) *Gaz. chim. ital.*, **76**, 182–6 (1946); (b) *ibid.*, **77**, 509–17, 518–25 (1947); (c) *Ital. pat.* 458,770 (1950)—C.A. **41**, 947; **42**, 5411, 5413; **45**, 9555.
491. Lamberto Malatesta and F. Laverone, *Gaz. chim. ital.*, **81**, 596–608 (1951)—C.A. **46**, 6079.
492. Lamberto Malatesta and Rachele Pizzoti, (a) *Chimica e industria (Milan)*, **27**, 6–10 (1945); (b) *Gaz. chim. ital.*, **76**, 167–81 (1946)—C.A. **40**, 7039; **41**, 2012.
493. Manchester Oxide Co., Ltd., Bernard Bann, Pavel Krug, D. E. Wheeler, Wallace Taylor, and Geoffrey Gladding, *Brit. pat.* 551,205, 551,206, 551,207 (1943); 559,384 (1946)—C.A. **38**, 1751; **40**, 368.
494. Y. A. Mandel'baum, I. L. Vladimirova, and N. N. Mel'nikov, *Zhur. Obshchei Khim.*, **23**, 429–32 (1953)—C.A. **48**, 3887.
495. F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **121**, 594–603 (1922)—C.A. **16**, 2110.
496. Anna Mannesier-Mameli, IX Congr. intern. quim. pura aplicada, **4**, 588–93 (1934)—C.A. **30**, 2949.
497. R. H. F. Manske, R. W. Beattie, and Marshall Kulka to U.S. Rubber Co., *U.S. pat.* 2,595,224 (1951)—C.A. **46**, 3566.
498. R. H. F. Manske and Marshall Kulka to U.S. Rubber Co., *U.S. pat.* 2,575,225 (1951)—C.A. **46**, 3566.
499. S. Marcovitch, *Com. Fertilizer*, **76**, No. 3, 14–7, 19 (1948)—C.A. **42**, 3898.
500. E. G. Marsden and Samuel Smiles, *J. Chem. Soc.*, **99**, 1353–8 (1911)—C.A. **5**, 3567.
501. Martin and Shaw, B10S Final Report No. 1095, Item 22, May–June 1946 (PB-78244).
502. T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Am. Chem. Soc.*, **67**, 1662–4 (1945)—C.A. **40**, 55.
503. E. J. Matheron, N. Y. State Flower Growers, *Bull.* No. **49**, 11–2 (1949)—C.A. **43**, 9338.
504. May & Baker Ltd. and J. H. Barber, *Brit. pat.* 550,446, 557,055 (1943)—C.A. **38**, 1850; **39**, 2296.
505. N. N. Mel'nikov and K. D. Shvetsova-Shilovskaya, *Doklady Akad. Nauk SSSR*, **86**, 543–6 (1952)—C.A. **48**, 556.

506. W. E. Messer to U.S. Rubber Co., U.S. pat. 2,257,974 (1942); 2,370,253 (1945)—C.A. 36, 930; 39, 3966.
507. R. L. Metcalf, Chem. Biol. Coordination Center, Natl. Res. Council, Washington, D.C. Rev., No. 1, 84 p. (1948)—C.A. 43, 5146.
508. R. L. Metcalf and R. B. March, (a) J. Econ. Entomol., 42, 721–8 (1949); (b) Science, 117, 527–8 (1953); J. Econ. Entomol., 46, 288–94 (1953)—C.A. 44, 3663; 47, 9550; 48, 4166.
509. Alwin Meuwsen, (a) Ber., 68, 121–7 (1935); (b) *ibid.*, 69, 935–7 (1936)—C.A. 29, 2506; 30, 5556.
510. Alwin Meuwsen and Hans Gebhardt, (a) Ber., 68, 1011–3 (1935); *ibid.*, 69, 937–46 (1936); (b) *ibid.*, 70, 792–6 (1937)—C.A. 29, 4733; 30, 5557; 31, 4643.
511. A. Michaelis, (a) Ann., 164, 9–45 (1872); (b) *ibid.*, 326, 162, 201–20 (1903); (c) Ber., 5, 6 (1872).
512. A. Michaelis, Edgar Mentzel, and Julius Hochhut, Ann., 407, 298–305 (1915)—C.A. 9, 1031.
513. W. W. Middlekauff, J. Econ. Entomol., 42, 840–1 (1949)—C.A. 44, 1640.
514. W. W. Middlekauff and A. E. Pritchard, J. Econ. Entomol., 42, 852 (1949)—C.A. 44, 1640.
515. L. A. Mikeska to S. O. Dev. Co., U.S. pat. 2,471,115 (1949)—C.A. 43, 5939.
516. L. A. Mikeska and Eugene Lieber to S. O. Dev. Co., U.S. pat. 2,321,307 (1943)—C.A. 37, 6885.
517. C. J. Miller and Samuel Smiles, J. Chem. Soc., 127, 224–33 (1925)—C.A. 19, 1133.
518. E. A. Moelwyn-Hughes, (a) Nature, 133, 294 (1934); (b) Trans. Faraday Soc., 37, 279–81 (1941)—C.A. 28, 2671; 35, 6177.
519. Monsanto Chemical Co., Brit. pat. 655,668 (1951)—C.A. 46, 8152.
520. M. L. Moore and T. B. Johnson, (a) J. Am. Chem. Soc., 57, 1287–9 (1935); (b) *ibid.*, 2234–6; (c) *ibid.*, 1517–19 (1935); *ibid.*, 58, 1091–4, 1960–1 (1936)—C.A. 29, 5821; 30, 89; 29, 7300; 30, 5952, 8185.
521. C. V. G. Morgan and R. S. Downing, Can. Entomol., 82, 44–9 (1950)—C.A. 44, 6565.
522. H. L. Morrill to Monsanto Chem. Co., U.S. pat. 2,601,219 (1952)—C.A. 46, 8322.

523. J. R. Morris to Texas Oil Co., U.S. pat. 2,417,562 (1947)—C.A. 41, 3613.
524. C. L. Moyle to Dow Chem. Co., (a) U.S. pat. 2,250,049 (1941); (b) 2,599,516 (1952); Brit. pat. 699,064 (1953); (c) U.S. pat. 2,615,037, 2,615,038 (1952)—C.A. 35, 7062; 46, 8322; 48, 4172; 47, 9343.
525. C. L. Moyle and E. P. Lubs to Dow Chem. Co., U.S. pat. 2,552,576 (1951)—C.A. 45, 9080.
526. D. H. Murray and J. W. T. Spinks, Can. J. Chem., 30, 497 (1952)—C.A. 47, 2725.
527. J. M. Musselman to S. O. Co. of Ohio, U.S. pat. 2,383,495 (1945)—C.A. 40, 730.
528. K. G. Naik and G. V. Jadhav, Quart. J. Indian Chem. Soc., 3, 260-72 (1926)—C.A. 21, 1967.
529. R. B. Neiswander, J. Econ. Entomol., 42, 41-4 (1949)—C.A. 43, 5526.
530. J. F. Nelson and L. A. Mikeska to S. O. Dev. Co., U.S. pat. 2,391,184 (1945)—C.A. 40, 3255.
531. E. J. Newcomer and F. P. Dean, (a) J. Econ. Entomol., 41, 691-4 (1948); (b) *ibid.*, 42, 857-8 (1949)—C.A. 43, 1523; 44, 1641.
532. J. H. Newton and G. M. List, J. Econ. Entomol., 42, 346-8 (1949)—C.A. 43, 7630.
533. A. H. Ney, U.S. pat. 1,723,295 (1929)—C.A. 23, 4433.
534. Kenneth Nolan and Frank Wilcoxon, Agr. Chemicals, 5, No. 1, 53, 74 (1950)—C.A. 44, 4192.
535. G. R. Norman, W. M. LeSuer, and T. W. Mastin, J. Am. Chem. Soc., 74, 161-3 (1952)—C.A. 47, 6862.
536. E. M. Nygaard, G. S. Crandall, and H. G. Berger, J. Inst. Petr., 27, No. 214, 348-68 (1941)—C.A. 36, 2389.
537. E. M. Nygaard, J. H. McCracken, and F. M. Seger to Socony-Vac. Oil Co., U.S. pat. 2,326,102 (1943)—C.A. 38, 469.
538. E. A. Oberright to Socony-Vac. Oil Co., U.S. pat. 2,589,326 (1952)—C.A. 46, 11227.
539. R. A. Ogg, Jr., Trans. Faraday Soc., 31, 1385-92 (1935)—C.A. 30, 338.
540. E. U. Ohsol, C. S. Carlson, and B. E. Hudson, Jr., to S. O. Dev. Co., U.S. pat. 2,575,290 (1951)—C.A. 46, 8144.
541. J. F. Olin to Sharples Chemicals Inc., U.S. pat. 2,650,240 (1953)—C.A. 48, 8819.
542. W. J. O'Neill, J. Econ. Entomol., 42, 636-9 (1949)—C.A. 44, 267.

543. B. A. Orkin to Socony-Vac. Oil Co., U.S. pat. 2,592,175 (1952)—C.A. 46, 8414.
544. W. L. Orr and Norman Kharasch, J. Am. Chem. Soc., 75, 6030–5 (1953)—C.A. 49, 1623.
545. J. L. Osborne to Am. Cyanamid Co., U.S. pat. 2,343,831 (1944)—C.A. 38, 3832.
546. M. R. Osburn, (a) J. Econ. Entomol., 42, 542 (1949); (b) *ibid.*, 557—C.A. 43, 7627; 44, 787.
547. Robert Otto, (a) Ann., 145, 317–29 (1868); (b) Ber., 13, 1282–3 (1880); (c) *ibid.*, 15, 121–32 (1882).
548. Robert Otto and Oscar von Gruber, Ann., 145, 10–25 (1868).
549. Robert Otto and Ernst Heydecke, Ber., 25, 1477–83 (1892).
550. Robert Otto, J. Löwenthal, and A. von Gruber, Ann., 149, 101–19 (1869).
551. Robert Otto and Adelbert Rössing, (a) Ber., 19, 1235–42 (1886); (b) *ibid.*, 3129–32 (1886); *ibid.*, 20, 2079–88 (1887); (c) *ibid.*, 25, 988–91 (1892).
552. Robert Otto and Julius Tröger, Ber., 26, 993–6 (1893).
553. G. D. Palmer and E. L. Costello—Unpublished.
554. J. R. Parker, Bur. Entomol. and Plant Quarantine, E-774, 18 p. (1949)—C.A. 43, 7185.
555. J. C. Patrick and R. C. Ellingson—Unpublished.
556. C. Pauly and R. Otto, (a) Ber., 9, 1639–41 (1876); (b) *ibid.*, 10, 2181–5 (1877); (c) *ibid.*, 11, 2070–2 (1878); (d) *ibid.*, 2073–5.
557. D. R. Peck, Chemistry & Industry, 1948, 526—C.A. 43, 1139.
558. C. J. Pederson and R. O. Bender to Du Pont Co., U.S. pat. 2,382,905 (1945)—C.A. 39, 5475.
559. N. E. Peery to Shell Dev. Co., U.S. pat. 2,223,793 (1940)—C.A. 35, 2315.
560. W. Penecke, U.S. pat. 1,615,646 (1926)—C.A. 21, 825.
561. G. W. Perold and H. L. F. Snyman, J. Am. Chem. Soc., 73, 2379–80 (1951)—C.A. 46, 924.
562. A. Perret and R. Perrot, Bull. soc. chim., [5] 1, 1531–48 (1934)—C.A. 29, 2505.
563. B. K. Petty, (a) Farming in S. Africa, May 1948, 8 p. Reprint No. 23, June 1948; 7 p. Reprint No. 31; (b) *ibid.*, March 1949, 4 p. Reprint 23—C.A. 44, 1215, 3200.
564. Louis Peyron and Jacquelin Lapaine, Compt. rend., 227, 132–3 (1948)—C.A. 43, 2934.

565. P. S. Pishchimuka, (a) *Ber.*, 41, 3854-9 (1908); (b) *J. prakt. Chem.*, [2] 84, 746-60 (1911); (c) *J. Russ. Phys. Chem. Soc.*, 44, 1406-1554 (1912); (d) *ibid.*, 56, 11-4 (1925); *J. chim. Ukraine*, 1, 87-9—C.A. 3, 431; 6, 989; 7, 987; 19, 2808; 20, 2816.
566. H. M. Pitt and Wilburn Boggs to Stauffer Chem. Co., U.S. pat. 2,647,143 (1953)—C.A. 48, 8250.
567. V. M. Plets, *J. Gen. Chem. (USSR)*, 6, 1198-1202 (1936); 8, 1296-7 (1938)—C.A. 31, 1355; 33, 4193.
568. C. C. Plummer and J. G. Shaw, *J. Econ. Entomol.*, 42, 708-9 (1949)—C.A. 44, 1222.
569. J. B. Polivka, *J. Econ. Entomol.*, 43, 109 (1950)—C.A. 44, 5058.
570. D. W. Pound to Pest Control Ltd., *Brit. pat.* 668,536 (1952)—C.A. 47, 5438.
571. K. P. Powers to Gulf Res. and Dev. Co., U.S. pat. 2,203,-102 (1940)—C.A. 34, 7103.
572. W. G. Prescott and Samuel Smiles, *J. Chem. Soc.*, 99, 640-9 (1911)—C.A. 5, 3047.
573. T. S. Price and D. F. Twiss, (a) *Proc. Chem. Soc.*, 23, 263; *J. Chem. Soc.*, 91, 2021-31 (1907); *ibid.*, 93, 1645-53 (1908); *ibid.*, 95, 1050-5 (1909); (b) *ibid.*, 93, 1395-1400 (1908); (c) *ibid.*, 1401-5; (d) *ibid.*, 95, 1489-91 (1909)—C.A. 2, 816, 1601; 3, 2680, 2805; 2, 3064.
574. T. S. Price and D. F. Twiss, (a) *J. Chem. Soc.*, 95, 1489-91 (1909); (b) *ibid.*, 1725-9; (c) *ibid.*, 97, 1175-83 (1910); (d) *Ber.*, 41, 4375 (1908)—C.A. 4, 195, 750; 5, 1076; 3, 653.
575. A. E. Pritchard and R. E. Beer, *J. Econ. Entomol.*, 42, 372-9 (1949)—C.A. 43, 8088.
576. A. E. Pritchard, R. E. Beer, and R. G. Rosenstiel, *J. Econ. Entomol.*, 42, 845-6 (1949)—C.A. 44, 1640.
577. G. G. Pritzker, *Natl. Pet. News*, 37, R1001-10 (1945)—C.A. 40, 448.
578. W. A. Proell and W. B. Chilcote to S. O. of Indiana, U.S. pat. 2,598,013 (1952)—C.A. 47, 3332.
579. C. F. Prutton to Lubri-Zol. Corp., U.S. pat. 2,242,260 (1941)—C.A. 35, 6106.
580. Attilio Purgotti, *Gaz. chim. ital.*, 22, I, 416-26 (1892).
581. D. D. Questel and R. V. Connin, *J. Econ. Entomol.*, 40, 914-5 (1947)—C.A. 42, 2720.
582. D. D. Questel, R. V. Connin, and S. I. Gertler, U.S. Dept. Agr., Bur. Entomol. Plant Quarantine, E-785, 9 p. (1949)—C.A. 43, 9336.

583. C. F. Rainwater, *J. Econ. Entomol.*, 40, 923-5 (1947)—C.A. 42, 2710.
584. William Ramsey, *Ber.*, 8, 764 (1875).
585. B. Rathke, (a) *Ann.*, 161, 149-71 (1872); (b) *ibid.*, 167, 195-221 (1873); *Ber.*, 3, 858-62 (1870); *ibid.*, 5, 799 (1872); (c) *ibid.*, 19, 395-6 (1886); (d) *ibid.*, 21, 2539-45 (1888).
586. M. Raucourt, *Rev. Hort.*, 121, 48-9, 160-1 (1949)—C.A. 44, 4190.
587. W. J. Reid, Jr., and F. P. Cuthbert, Jr., U.S. Dept. Agr., Bur. Entomol. and Plant Quarantine, *E-787*, 17 p. (1949)—C.A. 44, 262.
588. O. M. Reiff to Socony-Vac. Oil Co., U.S. pat. 2,392,766 (1946)—C.A. 40, 2293.
589. O. M. Reiff and H. J. Andress, Jr., to Socony-Vac. Oil Co., (a) U.S. pat. 2,386,207 (1945); 2,480,673 (1949); (b) 2,438,876 (1948)—C.A. 40, 729; 43, 9432; 42, 5657.
590. Heinrich Rheinboldt, (a) *Ber.*, 59, 1311-3 (1926); (b) *Rev. brasil chim. (São Paulo)*, 4, 169-71 (1937)—C.A. 20, 2975; 32, 484.
591. Heinrich Rheinboldt, Martin Dewald, and Otto Diepenbruck, *J. prakt. Chem.*, [2] 130, 133-46 (1931)—C.A. 25, 3618.
592. Heinrich Rheinboldt and Ernest Giesbrecht, (a) *J. Am. Chem. Soc.*, 71, 1740-1 (1949); (b) *ibid.*, 72, 866-9 (1950); (c) *Ann.*, 568, 198-217 (1950); (d) *ibid.*, 574, 227-42 (1951)—C.A. 43, 8366; 45, 4213; 44, 8316; 47, 2129.
593. Heinrich Rheinboldt and Friedrich Mott, (a) *J. prakt. Chem.*, [2] 133, 328-30 (1932); (b) *Ber.*, 65, 1223-4 (1932); (c) *ibid.*, 72, 668-70 (1939)—C.A. 26, 3775, 5063; 33, 4959.
594. Heinrich Rheinboldt, Friedrich Mott, and Erwin Motzkus, *J. prakt. Chem.*, [2] 134, 257-81 (1932)—C.A. 26, 5544.
595. Heinrich Rheinboldt and Erwin Motzkus, *Ber.*, 72, 657-67 (1939)—C.A. 33, 4957.
596. Heinrich Rheinboldt and Madeleine Perrier, *Bull. soc. chim. France*, 1950, 245-53—C.A. 44, 8882.
597. Heinrich Rheinboldt, Franz Tappermann, and Hans Kleu, *J. prakt. Chem.*, [2] 153, 65-76 (1939)—C.A. 33, 6279.
598. W. C. Rhoades and C. H. Brett, *J. Kansas Entomol. Soc.*, 21, 66-70 (1948)—C.A. 42, 9049.
599. F. P. Richter and B. A. Orkin to Socony-Vac. Oil Co., U.S. pat. 2,590,039 (1952)—C.A. 46, 5892.

600. M. M. Richter, Ber., 49, 1026-9 (1916)—C.A. 11, 800.
601. P. O. Richter, J. Econ. Entomol., 42, 838-9 (1949)—C.A. 44, 1641.
602. Randolf Riemschneider, Anz. Schädlingkunde, 22, No. 1, 3 p. (1949). Reprint. C.A. 43, 7627.
603. R. W. Rings, (a) J. Econ. Entomol., 42, 701-2 (1949); (b) *ibid.*, 43, 70-2 (1950)—C.A. 44, 1221, 6565.
604. Arthur Roe and J. W. McGeehee, J. Am. Chem. Soc., 70, 1662 (1948)—C.A. 42, 5439.
605. M. T. Rogers and K. J. Gross, J. Am. Chem. Soc., 74, 5294-6 (1952)—C.A. 47, 1444.
606. Enrico Romano and Giorgio Giulimondi, Ann. sper. agrar. (Rome), (N.S.), 5, 1527-31 (1951)—C.A. 46, 5247.
607. C. J. Romieux to Am. Cyanamid Co., U.S. pat. 1,836,685 (1931)—C.A. 26, 1158.
608. C. J. Romieux and K. D. Ashley to Am. Cyanamid Co., (a) U.S. pat. 1,949,629 (1934), Reissue 20,411; (b) 2,226,514 (1941)—C.A. 28, 2948; 36, 2270.
609. C. J. Romieux and H. P. Wohnsiedler to Am. Cyanamid Co., U.S. pat. 1,748,619 (1930)—C.A. 24, 1868.
610. J. N. Roney, J. Econ. Entomol., 42, 555 (1949)—C.A. 44, 783.
611. Raphael Rosen to S. O. Dev. Co., U.S. pat. 2,261,290 (1941)—C.A. 36, 1166.
612. Luigi Rosnati, (a) Gaz. chim. ital., 75, 225-32 (1945); (b) *ibid.*, 76, 272-82 (1946)—C.A. 41, 4097; 42, 876.
613. H. W. Rudel and J. I. Wasson to S. O. Dev. Co., U.S. pat. 2,645,657 (1953)—C.A. 47, 10217.
614. P. Rudert, Ber., 26, 565-95 (1893).
615. J. T. Rutherford and R. J. Miller to S. O. Co. of Calif., U.S. pat. 2,252,984, 2,252,985 (1941)—C.A. 35, 8282.
616. P. L. Salzberg to Du Pont Co., (a) U.S. pat. 2,121,611 (1938); (b) 2,178,610 (1939)—C.A. 32, 6363; 34, 1476.
617. P. L. Salzberg and J. H. Werntz to Du Pont Co., U.S. pat. 2,063,629 (1936)—C.A. 31, 702.
618. Giuseppi Sanna and Spano Stefano, Gaz. chim. ital., 72, 305-12 (1942)—C.A. 38, 3953.
619. A. L. Scales and G. L. Smith, J. Econ. Entomol., 41, 403-5 (1948)—C.A. 42, 9051.
620. George Scatchard, J. Chem. Phys., 7, 657-63 (1939)—C.A. 33, 8092.
621. M. S. Schechter and H. L. Haller, J. Am. Chem. Soc., 63, 1764-5 (1941)—C.A. 35, 5461.

622. Günter Scheibe and Otto Stoll, Ber., 71, 1571-5 (1938)—C.A. 32, 8270.
623. R. Schiller and R. Otto, Ber., 9, 1637 (1876).
624. Erik Schirm to "Unichem" Chemikalien Handels, U.S. pat. 2,012,073 (1935)—C.A. 29, 6670.
625. Otto Schmidt, Ber., 40, 865-73 (1907)—C.A. 1, 1388.
626. Erich Schneider, Ber., 84, 911-6 (1951)—C.A. 46, 6585.
627. Alfons Schöberl, Ber., 70, 1186-93 (1937)—C.A. 31, 5762.
628. Alfons Schöberl and T. Horning, Ann., 534, 210-25 (1938)—C.A. 32, 8459.
629. Alfons Schöberl and Ernst Ludwig, Ber., 70, 1422-32 (1937)—C.A. 31, 6199.
630. Alfons Schöberl and Paul Rambacker, Ann., 538, 84-98 (1939)—C.A. 33, 6245.
631. Alexander Schönberg, O. Schütz, and J. Peter, Ber., 62, 1663-70 (1929)—C.A. 24, 88.
632. Alexander Schönberg and T. Stolpp, Ber., 63, 3102-16 (1930)—C.A. 25, 2413.
633. Gerhard Schrader to Farbenfabriken Bayer, (a) U.S. pat. 2,571,989 (1951); (b) 2,597,534 (1952); (c) 2,624,745 (1953)—C.A. 46, 3066; 47, 5357, 8092.
634. Gerhard Schrader and Hans Kukenthal to Farbenfabriken Bayer, U.S. pat. 2,583,744 (1952)—C.A. 46, 3710.
635. J. C. Schread, J. Econ. Entomol., 41, 318-24 (1948); *ibid.*, 42, 383-7 (1949)—C.A. 42, 7922; 43, 9346.
636. W. A. Schulze to Phillips Pet. Co., U.S. pat. 2,123,082 (1938)—C.A. 32, 6667.
637. Felix Schwarze, J. prakt. Chem., [2] 10, 222-35 (1874).
638. Alfred Schwicker, Ber., 22, 1733-4 (1889).
639. D. B. Scott, Jr., J. Econ. Entomol., 42, 782-5 (1949)—C.A. 44, 1222.
640. W. L. Seamon to B. F. Goodrich Co., U.S. pat. 2,355,335 (1944)—C.A. 38, 6302.
641. F. M. Seger and E. M. Nygaard to Socony-Vac. Oil Co., U.S. pat. 2,329,489 (1943)—C.A. 38, 1094.
642. F. R. Shaw and G. D. Butler, J. Econ. Entomol., 42, 855-6 (1949)—C.A. 44, 1641.
643. Franklin Sherman, III and H. L. King, J. Econ. Entomol., 41, 807-8 (1948)—C.A. 43, 1523.
644. B. H. Shoemaker and C. M. Loane to S. O. Co. of Ind., (a) U.S. pat. 2,160,917 (1939); (b) 2,191,996 (1940)—C.A. 33, 7553; 34, 4378.
645. R. L. Shuman to Celluloid Corp., U.S. pat. 2,133,310 (1938)—C.A. 33, 645.

646. G. A. Silvey and G. H. Cady, *J. Am. Chem. Soc.*, **72**, 3624-6 (1950); *ibid.*, **74**, 5792-3 (1952)—C.A. **44**, 9851; **48**, 4782.
647. A. Simon and G. Schulze, *Naturwissenschaften*, **25**, 669 (1937); *Z. anorg. allgem. Chem.*, **242**, 313-68 (1939)—C.A. **32**, 427; **34**, 1563.
648. Arthur Slater, *J. Chem. Soc.*, **85**, 1286-1304 (1904).
649. L. D. Small, J. H. Bailey, and J. C. Cavallito, (a) *J. Am. Chem. Soc.*, **69**, 1710-3 (1947); (b) *ibid.*, **71**, 3565-6 (1949)—C.A. **41**, 6196; **44**, 1011.
650. Samuel Smiles and D. T. Gibson, *J. Chem. Soc.*, **125**, 176-83 (1924)—C.A. **18**, 978.
651. Bengt Smith and Sune Delin, *Svensk Kem. Tid.*, **65**, 10-6 (1953) (in English)—C.A. **48**, 578.
652. C. F. Smith, I. D. Jones, and L. D. Calvin, *J. Econ. Entomol.*, **43**, 179-81 (1950)—C.A. **44**, 6075.
653. C. F. Smith, I. D. Jones, and J. A. Rigney, *J. Econ. Entomol.*, **42**, 618-23 (1949)—C.A. **44**, 267.
654. F. F. Smith, *J. Econ. Entomol.*, **41**, 955-9 (1948)—C.A. **43**, 5148.
655. F. F. Smith and A. L. Boswell, *North Am. Gladiolus Council Bull. No. 13*, **32**, **34**, **36**, **78** (1948)—C.A. **42**, 2716.
656. F. F. Smith, Philip Brierley, and R. A. Fulton, *Proc. Am. Soc. Hort. Sci.*, **51**, 327-32 (1948)—C.A. **43**, 1523.
657. F. F. Smith and R. A. Fulton, *Florists Exchange Hort. Trade World*, **113**, No. **23**, **15**, 49-51 (1949)—C.A. **44**, 3658.
658. F. F. Smith, R. A. Fulton, and P. H. Lung, *J. Econ. Entomol.*, **41**, 624-31 (1948)—C.A. **43**, 1523.
659. F. F. Smith, P. H. Lung, and R. A. Fulton, *U.S. Dept. Agr., Bur. Entomol. and Plant Quarantine, E-759*, **8** p. (1948)—C.A. **42**, 810.
660. G. E. P. Smith, Jr., to Firestone Tire and Rubber Co., U.S. pat. 2,367,827 (1945); 2,581,932 (1952)—C.A. **39**, 3690; **46**, 3792.
661. H. G. Smith, T. L. Cantrell, and M. L. Hill to Gulf Oil Corp., U.S. pat. 2,447,288 (1948)—C.A. **43**, 665.
662. R. H. Smith, *J. Chem. Soc.*, **22**, 302-4 (1869).
663. J. A. Smythe, *J. Chem. Soc.*, **121**, 1400-5 (1922)—C.A. **16**, 3078.
664. O. I. Snapp, (a) *J. Econ. Entomol.*, **41**, 569-74 (1948); (b) *ibid.*, **42**, 7-11 (1949)—C.A. **43**, 1143, 5527.
665. Soc. chim. à Bale, *Brit. pat.* 537,221 (1941); *Swiss pat.* 212,401 (1941)—C.A. **36**, 1334, 3686.

666. Socony-Vacuum Oil Co., (a) Brit. pat. 610,056 (1948)—C.A. 43, 1803; (b) Report.
667. M. B. Sparke, J. L. Cameron, and Norman Kharasch, J. Am. Chem. Soc., 75, 4907–10 (1953)—C.A. 48, 12697.
668. W. Spring, Ber., 7, 1162–3 (1874).
669. W. Spring and E. Legros, Ber., 15, 946, 1938–40 (1882).
670. E. M. Stafford, J. Econ. Entomol., 42, 656–60 (1949)—C.A. 44, 1222.
671. Hellmuth Stamm, Ber., 68, 673–6 (1935)—C.A. 29, 4327.
672. Hellmuth Stamm and Margot Goehring, Ber., 76, 737–42 (1943)—C.A. 38, 2579.
673. Hellmuth Stamm and Hellmut Wintzer, (a) Ber., 70, 2058–60 (1937); (b) *ibid.*, 71, 2212–9 (1938)—C.A. 32, 1993; 33, 1618.
674. Standard Oil Dev. Co., (a) Fr. pat. 853,052 (1940); (b) Brit. pat. 586,333 (1947); (c) 666,636 (1952)—C.A. 36, 2392; 41, 6709; 46, 11232.
675. J. W. Starrett to S. O. Co. of Ind., Can. pat. 461,503 (1949)—C.A. 44, 5585.
676. Wilhelm Steinkopf and Siegfried Müller, Ber., 56, 1926–30 (1923)—C.A. 18, 525.
677. Sterling Drug Inc., Brit. pat. 654,390 (1951)—C.A. 46, 523.
678. D. R. Stevens and R. S. Spindt to Gulf Res. & Dev. Co., U.S. pat. 2,542,370 (1951)—C.A. 45, 5712.
679. H. Stevenson and Samuel Smiles, J. Chem. Soc., 1931, 718–23—C.A. 25, 3338.
680. J. M. Stewart and C. H. Burnside, J. Am. Chem. Soc., 75, 243–4 (1950)—C.A. 48, 110.
681. J. M. Stewart and H. P. Cordts, J. Am. Chem. Soc., 74, 5880–4 (1952)—C.A. 48, 1263.
682. L. L. Stitt and James Evanson, J. Econ. Entomol., 42, 614–7 (1949)—C.A. 44, 1218.
683. G. G. Stoner and Gregg Dougherty, J. Am. Chem. Soc., 63, 987–8, 1481 (1941)—C.A. 35, 3604, 4365.
684. J. Strating and H. J. Backer, Rec. trav. chim., 69, 638–48 (1950)—C.A. 44, 7222.
685. Danella Straup and E. J. Cohn, J. Am. Chem. Soc., 57, 1794–1800 (1935)—C.A. 30, 355.
686. Wilhelm Strecker and Charlotte Grossmann, Ber., 49, 63–87 (1916)—C.A. 10, 897.
687. Wilhelm Strecker and H. Heuser, Ber., 57, 1364–72 (1924)—C.A. 18, 3567.

688. Wilhelm Strecker and Rudolph Spitaler, Ber., 59, 1754-75 (1926)—C.A. 26, 1932.
689. R. E. Stutz and R. L. Shriner, J. Am. Chem. Soc., 55, 1242-5 (1933)—C.A. 27, 1861.
690. I. F. Suknevich, A. A. Chilingaryan, and M. D. Sergeenko, Russ. pat. 35,191 (1934)—C.A. 29, 8001.
691. F. W. Sullivan, Jr., to S. O. Co. of Ind., U.S. pat. 2,174,019 (1939)—C.A. 34, 1166.
692. E. S. Sylvester, J. Econ. Entomol., 42, 766-9 (1949)—C.A. 44, 1640.
693. W. G. Taggart and I. L. Forbes, Louisiana Agr. Exptl. Sta. Ann. Rept., 1947-8, 3-153 (1949)—C.A. 43, 6774.
694. E. F. Taschenberg, (a) J. Econ. Entomol., 42, 629-32 (1949); (b) *ibid.*, 43, 76-81 (1950); (c) N. Y. Agr. Exptl. Sta. (Geneva), Bull. No. 736, 21 p. (1949)—C.A. 44, 1221, 6565, 3200.
695. H. S. Tasker and H. O. Jones, J. Chem. Soc., 95, 1910-8 (1909)—C.A. 4, 1023.
696. Jan Teppema, Can. pat. 331,864 (1933)—C.A. 27, 3950.
697. H. A. Thiemann, Am. Ind. Hyg. Assoc. Quart., 10, 10-5 (1949)—C.A. 43, 9353.
698. W. L. Thompson and J. T. Griffiths, Citrus Ind., 29, No. 3, 4, 10; *ibid.*, No. 4, 18-9, 26 (1948)—C.A. 42, 7922.
699. W. L. Thompson, C. R. Stearns, and J. T. Griffiths, Jr., Citrus Ind., 30, No. 3, 5-8, 12, 14 (1949)—C.A. 43, 9349.
700. Thurston, FIAT Final Report No. 949, Oct. 14, 1946 (PB-60890).
701. Howard Tieckelmann and H. W. Post, J. Org. Chem., 13, 265-7 (1948)—C.A. 42, 4946.
702. A. N. Tissot and L. C. Kuitert, Florida Entomologist, 31, 105-12 (1948)—C.A. 43, 3136.
703. Gerrit Toennies, J. Biol. Chem., 122, 27-47 (1937)—C.A. 32, 1655.
704. Gerrit Toennies and T. F. Lavine, J. Biol. Chem., 105, 107-13, 115-21 (1934); 113, 571-82 (1936); U.S. pat. 2,078,592 (1937)—C.A. 28, 4036; 30, 3842; 31, 4344.
705. Henry Tolkmith to Dow Chem. Co., U.S. pat. 2,592,617, 2,592,618, 2,592,619, 2,592,620, 2,592,621 (1952)—C.A. 46, 11249.
706. James Toman, Growth 3, 419-25 (1940)—C.A. 34, 4469.
707. A. D. F. Toy, J. Am. Chem. Soc., 73, 4670-4 (1951)—C.A. 46, 7697.

708. A. D. F. Toy and T. M. Beck to Victor Chem. Wks., U.S. pat. 2,471,464 (1949)—C.A. 43, 6659.
709. C. E. Trautman to Gulf Res. and Dev. Co., U.S. pat. 2,257,871, 2,257,872 (1941)—C.A. 36, 896.
710. B. V. Travis, *J. Econ. Entomol.*, 42, 451-7 (1949)—C.A. 44, 264.
711. J. Tröger and F. Hurdelbrink, *J. prakt. Chem.*, [2] 65, 83 (1902).
712. E. Tschunkur and H. Köhler to I. G. Farben., U.S. pat. 2,045,888 (1936)—C.A. 30, 5592.
713. Neely Turner, *J. Econ. Entomol.*, 42, 561-2 (1949)—C.A. 44, 267.
714. R. A. Turner and Ralph Connor, *J. Am. Chem. Soc.*, 69, 1009-12 (1947)—C.A. 41, 4781.
715. D. F. Twiss, *J. Chem. Soc.*, 105, 36-9 (1914)—C.A. 8, 1712.
716. E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, 75, 3523-6 (1953)—C.A. 48, 11346.
717. H. H. Velbinger, *Pharmazie*, 4, 165-76 (1949)—C.A. 43, 6776.
718. Guy Viel and Pierre Grison, *Compt. rend.*, 226, 840-1, 1843-5 (1948)—C.A. 42, 5606, 7922.
719. Mario Volpi, *Ann. sper. agrar. (Rome)*, (N.S.) 5, 1511-25 (1951)—C.A. 46, 5247.
720. D. Vörländer and E. Mittag, *Ber.*, 52, 413-23 (1919)—C.A. 13, 2363.
721. Theodor Wagner-Jauregg, Theodor Lennartz, and Hilde Kothny, *Ber.*, 74, 1513-21 (1941)—C.A. 37, 133.
722. K. C. Walker, *Advances in Chem. Ser., No. 1*, 123-7 (1950)—C.A. 44, 7008.
723. J. C. Ward, *Pests*, 16, No. 3, 34 (1948)—C.A. 42, 9046.
724. L. A. Warren and Samuel Smiles, *J. Chem. Soc.*, 1932, 1040-7—C.A. 26, 3500.
725. M. J. Way, *Chemist Druggist*, 150, 545-6 (1948)—C.A. 43, 1139.
726. C. R. Weaver, *J. Econ. Entomol.*, 43, 7-11 (1950)—C.A. 44, 5513.
727. R. L. Webster, *J. Econ. Entomol.*, 41, 677-83 (1948); *Washington Agr. Expt. Sta. Cir. No. 64*, 51 p. (1950)—C.A. 43, 1897; 44, 5511.
728. G. P. Wene, (a) *J. Econ. Entomol.*, 41, 514-5 (1948); (b) *ibid.*, 42, 73-6 (1949)—C.A. 42, 9049; 43, 5897.

729. G. P. Wene and R. A. Blanchard, *J. Econ. Entomol.*, **43**, 1-4 (1950)—C.A. **44**, 5513.
730. H. E. Westlake, Jr., and Gregg Dougherty, (a) *J. Am. Chem. Soc.*, **63**, 658-9 (1941); (b) *ibid.*, **64**, 149-50 (1942); (c) *ibid.*, **67**, 1861 (1945)—C.A. **35**, 2855; **36**, 1293; **40**, 70.
731. W. E. Westlake and J. E. Fahey, *Advances in Chem. Ser., No. 1*, 117-22 (1950)—C.A. **44**, 7008.
732. C. N. White to S. O. Co. of Ind., U.S. pat. 2,316,091 (1943)—C.A. **37**, 5858.
733. G. N. White, *J. Chem. Soc.*, **113**, 608-9 (1918)—C.A. **12**, 2193.
734. W. E. White and Archie Hood, *J. Am. Chem. Soc.*, **74**, 853-4 (1952)—C.A. **47**, 9905.
735. F. T. Whitworth, U.S. pat. 1,593,232 (1926)—C.A. **20**, 3152.
736. H. Wichelhaus, *Ann., Supl.* **6**, 257-80 (1868).
737. H. J. Wichmann, *J. Assoc. Offic. Agr. Chemists*, **31**, 349-52 (1948)—C.A. **42**, 8981.
738. C. F. Wight and Samuel Smiles, *J. Chem. Soc.*, **1935**, 340-3—C.A. **29**, 3321.
739. E. F. Williams, *Ind. Eng. Chem.*, **43**, 950-4 (1951)—C.A. **46**, 54.
740. J. W. Wilson, E. G. Kelsheimer, J. T. Griffiths, and A. N. Tissot, *Florida Entomologist*, **30**, 45, 47-56 (1948)—C.A. **42**, 6488.
741. M. C. Wilson, (a) *Proc. Indiana Acad. Sci.*, **57**, 111-2 (1948); (b) *J. Econ. Entomol.*, **42**, 496-8 (1949)—C.A. **43**, 4416; **44**, 788.
742. C. W. Wingo and G. W. Thomas, *J. Econ. Entomol.*, **41**, 688-91 (1948)—C.A. **43**, 1522.
743. Gene Wise and H. P. Lankelma, *J. Am. Chem. Soc.*, **74**, 529-31 (1952)—C.A. **47**, 8634.
744. R. S. Woglum, C. C. Plummer, and J. G. Shaw, *Calif. Citrograph*, **34**, 146, 177-80 (1949)—C.A. **43**, 3555.
745. W. F. Wolff and C. E. Johnson to S. O. Co. of Indiana, U.S. pat. 2,615,057 (1952)—C.A. **47**, 1376.
746. Leon Wolinski, Howard Tieckelmann, and H. W. Post, *J. Org. chem.*, **16**, 395-8, 1134-7, 1138-42 (1951)—C.A. **46**, 423, 3490.
747. J. L. Wood and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 2674-81 (1940)—C.A. **34**, 7901.
748. S. R. Wood to Cities Service Oil Co., U.S. pat. 2,484,061 (1949)—C.A. **44**, 4923.

- 749. D. E. Worrall, *J. Am. Chem. Soc.*, **52**, 2933-7 (1930)—C.A. **24**, 4018.
- 750. Y. Wuyts and A. Vangindertaelen, *Bull. soc. chim. Belg.*, **30**, 323-8 (1921)—C.A. **16**, 3077.
- 751. Yasuhida Yukawa, Fukuyasu Tokuda, and Shozo Amano, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **73**, 498-50 (1952)—C.A. **48**, 2000.
- 752. A. Zaucker and M. Bögemann, U.S. pat. 1,942,790; Re-issue 19,286 (1934)—C.A. **28**, 1892.
- 753. H. Zeumer and W. Fischer, *Z. anal. Chem.*, **135**, 401-9 (1952)—C.A. **46**, 9243.
- 754. T. Zincke, *Ber.*, **44**, 769-71 (1911)—C.A. **5**, 1914.
- 755. T. Zincke and K. Arnold, *Ber.*, **50**, 116-26 (1917)—C.A. **11**, 2789.
- 756. T. Zincke and Johanna Baeumer, *Ann.*, **416**, 86-112 (1918)—C.A. **13**, 575.
- 757. T. Zincke and A. Dahm, *Ber.*, **45**, 3457-68 (1912)—C.A. **7**, 2392.
- 758. T. Zincke and K. Eismayer, *Ber.*, **51**, 751-67 (1918)—C.A. **13**, 449.
- 759. T. Zincke and F. Farr, *Ann.*, **391**, 55-6, 57-88 (1912)—C.A. **6**, 2937.
- 760. T. Zincke and W. Frohneberg, (a) *Ber.*, **42**, 2721-36 (1909); (b) *ibid.*, **43**, 837-48 (1910)—C.A. **3**, 2577; **4**, 1746.
- 761. T. Zincke and O. Krüger, *Ber.*, **45**, 3468-79 (1912)—C.A. **7**, 2393.
- 762. T. Zincke and S. Lenhardt, *Ann.*, **400**, 1-27 (1913)—C.A. **7**, 3746.
- 763. T. Zincke and H. Röse, *Ann.*, **406**, 103-26, 127-37 (1914)—C.A. **9**, 54, 55.
- 764. T. Zincke and T. Schütz, *Ber.*, **45**, 471 (1912)—C.A. **6**, 1295.

CHAPTER 4.

Substituted Mercaptans

Theoretically, at least, the alkyl or aryl group of a mercaptan may carry any sort of substituent. However, only a few of these are important. There may be two or more substituents, of the same or of different kinds. The hydroxymercaptans are the best known. Halogenated mercaptans are known, but are not easy to prepare or to keep.

The substituent groups that are here considered are the hydroxyl, HO-, alkoxyl, RO-, or aroxyl, ArO-, alkylmercapto, RS-, or arylmercapto, ArS-, amino or substituted amino, NH₂-, NHR-, NHAr, NR₂ or NAr₂, and the carbonyl, -CO-. Hydroxymercaptans and chloro-mercaptans are so closely associated in preparations that they will be considered together.

Hydroxymercaptans

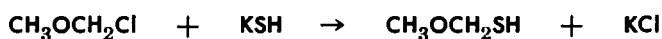
In general, these can be prepared by the usual methods and show the characteristic reactions of mercaptans. In some cases special methods are available. Their physical properties are a cross between those of alcohols and mercaptans.

HYDROXYMETHYL-MERCAPTAN AND DERIVATIVES

The simplest possible member of the group, hydroxymethyl mercaptan, HOCH₂SH, has not been isolated, but is believed to

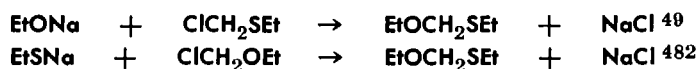
be produced when formaldehyde sulfoxylate is reduced by hypophosphorus acid.⁴³ The thioacetate, AcSCH_2OH , has been reported.⁵⁰

The methyl ether has been prepared:²⁵¹



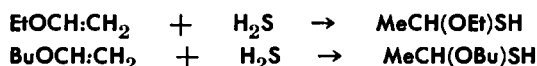
It is far more stable than the corresponding alcohol, $\text{CH}_3\text{OCH}_2\text{OH}$. It forms mercaptides and can be acetylated in pyridine.

The monothioformals are the dialkyl derivatives of hydroxymethyl mercaptan. They can be made in two ways:



These will be taken up under mercaptals in Chapter 13.

α -Hydroxymercaptan, or α -mercaptoethanol, $\text{MeCH}(\text{OH})\text{SH}$, is not known, but its ethers are made by the addition of hydrogen sulfide, in the presence of sulfur dioxide, to vinyl ethers:



These being hemiacetals are not very stable, but their acetates and benzoates, $\text{MeCH}(\text{OR})\text{SAc}$ and $\text{MeCH}(\text{OR})\text{SBz}$, are stable.^{345, 409}

Trifluoromethyl mercaptan, F_3CSH , has been obtained by treating the mercaptide, $(\text{F}_3\text{CS})_2\text{Hg}$, with hydrochloric acid. The sulfide, $(\text{F}_3\text{C})_2\text{S}$, and trifluoromethane are among the products of its decomposition by ultraviolet light. Chlorine converts it to the disulfide, $(\text{F}_3\text{CS})_2$. The mercaptan is hydrolyzed slowly in water and rapidly in alkaline solution.¹⁹⁸

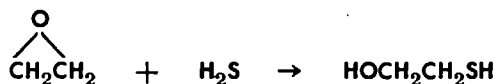
Trichloromethyl mercaptan, Cl_3CSH , has been prepared indirectly from perchloromercaptan, Cl_3CSCl , which has been considered in Chapter 3.⁹⁴

HYDROXYETHYL-MERCAPTAN

Monothioethylene glycol, β -mercaptoethanol, or β -hydroxyethyl mercaptan, $\text{HOCH}_2\text{CH}_2\text{SH}$, is the best known hydroxymercaptan. It was first made from ethylene chlorohydrin and sodium sulfhydrate.^{34a, 34b, 37, 71b, 303, 371} It may be obtained by the reduction of the disulfide, $(\text{HOCH}_2\text{CH}_2\text{S})_2$ from chlorhydrin

and sodium disulfide.^{147, 327a, 332} It and its homolog, 3-mercapto-propanol, have been prepared by the thiourea method.³¹⁹

The preferred method for making β -hydroxy-mercaptan is the reaction of ethylene oxide with hydrogen sulfide:



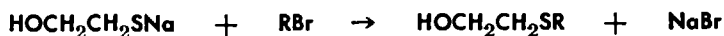
A second molecule of ethylene oxide reacts with mercaptoethanol to give thiodiglycol, $\text{S}(\text{CH}_2\text{CH}_2\text{OH})_2$. As the sulfhydryl group is more reactive than the hydroxyl, the hydrogen sulfide must be kept in excess. The reaction of ethylene oxide is said to be facilitated by the presence of water or the lower alcohols and by catalysts, such as porous clay and alumina.^{82, 83, 309, 492c} The yield of mercaptoethanol is practically quantitative when ethylene oxide and hydrogen sulfide are passed over iron or aluminum sulfide⁴⁶⁷ or alumina²⁹¹ at 300 to 400°. Hydrogen sulfide and ethylene oxide are introduced separately into alcohol containing some sodium ethylate, kept at 50 to 60°. The gross yield is high, 60% of it being mercaptoethanol and the rest thiodiglycol.^{492a} The yield of monothioglycol is said to be 71% when ethylene oxide and two equivalents of hydrogen sulfide are led into thiodiglycol at 30 to 35°.¹⁸⁹

Mercaptoethanol may be formed also by the reaction of ethylene sulfide with water:^{312a}



2-Hydroxymercaptan, or 2-mercaptoethanol, has two sets of reactions which are more or less independent of each other. As a mercaptan it forms mercaptides. The acid strength has been compared with that of thiophenol.³⁷² The sodium and potassium mercaptides are deliquescent solids. Those of the heavy metals are much like the corresponding compounds with other mercaptans. Some of those known are the mercuric, m. 123°, $\text{HOCH}_2\text{CH}_2\text{SHgCl}$, m. 135–40°, lead, m. 110°, cadmium, m. 139°, aurous, platinous, cuprous, nickel, bismuth, m. 79°, and antimony, m. 131°.^{34b}

The alkali mercaptides react with alkyl halides in the usual way:



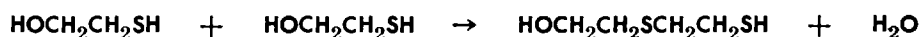
The rate of reaction with iodoacetamide has been compared with those of other mercaptides.⁴¹⁸

Mercaptoethanol forms either oxygen or sulfur esters according to conditions. In acid catalyzed esterification the oxygen ester is favored. With one equivalent of alkali and an acid chloride or anhydride the sulfur ester is formed. Polymeric esters with dibasic acids are claimed.³²⁸ The thioacetate, $\text{AcSCH}_2\text{-CH}_2\text{OH}$, may undergo self-alcoholysis to the acetate, $\text{HSCH}_2\text{-CH}_2\text{OAc}$. In dilute alkali, this acetate loses acetic acid to give ethylene sulfide.^{299d} The diacetate is pyrolyzed to vinyl thiol-acetate:¹⁴⁸

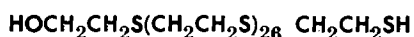


With aldehydes, mercaptals are formed in preference to acetals. Benzaldehyde gives the mercaptal, $\text{PhCH(SCH}_2\text{CH}_2\text{OH)}_2$.¹⁴⁷ The formal, $\text{CH}_2(\text{SCH}_2\text{CH}_2\text{OH})_2$, is obtained directly from hydroxyethyl thiosulfate.⁴⁸⁴ Spiro compounds are obtained from its reactions with α,α' -dichloroketones and with chloracetyl chloride.¹⁴

Heated with an acid, self-condensation of mercaptoethanol takes place with the elimination of water:



As the new molecule has the same end groups, this process can continue indefinitely. White solids are obtained. One of these melted at 177 to 180° and had an average molecular weight of 1720 which would correspond to the condensation of twenty-eight molecules of mercaptoethanol with the elimination of twenty-seven molecules of water. The product is a linear polymer and the average molecule would be:



The character of the polymer depends on the conditions of heating.³⁵³ Dehydration of mercaptoethanol with zinc chloride gives dithiane:^{34b}



It is oxidised by air slowly in phosphate-buffered solutions. It is a reducing agent for disulfide linkages in proteins.³¹⁸ Its oxidation potential, equilibrium constant, and free energy have been

compared with those of other mercaptans.³⁷⁷ Like any other mercaptan, it can be titrated with iodine. A colorimetric determination is based on the red color produced when sodium nitrite is added to it in alcoholic solution.^{374, 492b}

It shows an absorption band in the infrared.⁴⁶⁰ Its toxicity has been studied.⁴¹⁷

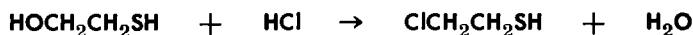
Mercaptoethanol can be added to unsaturates.^{312b} Among mercaptans, it is outstanding in this respect. With many unsaturates, the addition takes place spontaneously with the evolution of considerable heat. For example, when 78 g. is poured into 58 g. of allyl alcohol, 1 mole of each, the temperature rises 50° in about a minute.³⁵³ This spontaneous addition does not take place if sulfur is added to the mercaptoethanol but is not hindered by sulfur in the allyl alcohol.

Mercaptoethanol and thioglycolic acid solubilize keratin.²²⁸ This may be attributed to interchange with the cystine disulfide groups. This sort of reactions will be discussed under disulfides. Mercaptoethanol induces the coagulation of proteins.²⁰⁹

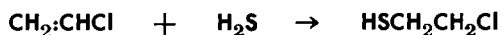
The ether, $O(CH_2CH_2SH)_2$, cannot be made directly from mercaptoethanol since, as mentioned before, its dehydration takes another course. It has been prepared by the thiourea method from dichloroethyl ether.^{12, 211} The germanium mercaptide, $[O(CH_2CH_2S)_2]_2Ge$ melts at 159.5°. ¹² A nickel complex is light brown.¹⁹¹ Eutectics of its thiobenzoate with related compounds have been studied.³⁶⁰ This dimercaptoether can be used with sulfur to vulcanize rubber.²¹¹

Haloethyl-Mercaptans

β -Chloroethyl mercaptan, $ClCH_2CH_2SH$, can be prepared from mercaptoethanol and hydrogen chloride: ^{34b}



The hydroxyl, being in the β -position to a sulfur atom, is easily replaced. It is seldom used in syntheses since it reacts so readily with itself, besides being disagreeable to handle. The same compound results from the addition of hydrogen sulfide to vinyl chloride: ⁴⁶⁹



This reaction is activated by ultraviolet light.⁴⁶⁹ The reaction of hydrogen chloride with ethylene sulfide gives the same product:^{107, 297}



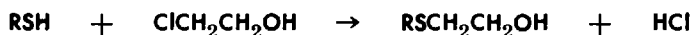
A second molecule may react to give the chlorosulfide mercaptan, $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$.¹⁰⁷ β -Chloroethyl mercaptan is vesicant and highly reactive. When it is agitated with sodium bicarbonate solution it reverts to ethylene sulfide. Under slightly different conditions, the product is polymeric ethylene sulfide, $(\text{CH}_2\text{-CH}_2\text{S})_n$.^{312b}

Similarly, ethylene sulfide and hydrogen bromide form β -bromoethyl mercaptan, $\text{BrCH}_2\text{CH}_2\text{SH}$.¹⁰⁷

The corresponding fluoroethyl mercaptan, $\text{FCH}_2\text{CH}_2\text{SH}$, is made by the addition of thioacetic acid to vinyl fluoride, followed by alcoholysis of the thioacetate.¹²² It has been prepared also from 2-fluoroethyl bromide and sodium hydrosulfide.²⁸⁴

The thioacetate, $\text{AcSCH}_2\text{CH}_2\text{I}$, of the iodo mercaptan results from the reaction of acetyl iodide on ethylene sulfide. It combines with trimethylamine to give thioacetylcholine iodide.²²⁴

As will be pointed out in the chapter on substituted sulfides, there has been much interest in β -chloroalkyl sulfides. It is more convenient to prepare the hydroxysulfide:



The hydroxyl group is replaced by chlorine as the final step.^{35, 37}

Alkoxyethyl-Mercaptans

The ethers, $\text{ROCH}_2\text{CH}_2\text{SH}$, cannot be obtained directly from mercaptoethanol, but are synthesized by the usual methods for mercaptans, from a chloride, $\text{ROCH}_2\text{CH}_2\text{Cl}$, and alkali hydrosulfide^{66, 174, 272, 298, 369, 445} or thiourea,³¹⁹ or from the hydrolysis of a thiolacetate.^{75, 414c} Sodium phenate and ethylene sulfide give the phenyl ether, $\text{PhOCH}_2\text{CH}_2\text{SH}$.³¹⁴ It was shown before that the addition of hydrogen sulfide to butyl vinyl ether, in the presence of sulfur dioxide, gives $\text{MeCH}(\text{OBu})\text{SH}$. In pyridine the addition goes the other way to form $\text{BuOCH}_2\text{CH}_2\text{SH}$.³⁴⁴ The presence of oxygen favors this mode of addition. A number of β -ether-mercaptans have been made in this way. The mercury

derivatives, $\text{ROCH}_2\text{CH}_2\text{SHgCl}$, have satisfactory melting points: ethyl, m. 155.6° ; propyl, m. 137.5° ; *i*-propyl, m. 153.5° ; butyl, m. 138° ; *i*-butyl, m. 144.5° ; *i*-amyl, m. 126° ; octyl, m. 126° and cyclohexyl, m. 150.5° .^{344, 409}

OTHER HYDROXY-MERCAPTANS AND DERIVATIVES

The reaction of an alcohol with isobutylene sulfide gives a β -alkoxymercaptan, $\text{ROCMe}_2\text{CH}_2\text{SH}$.^{421a, 422b} With acetic anhydride and pyridine, the diacetate, $\text{AcSCMe}_2\text{CH}_2\text{OAc}$, is obtained and with thioacetic acid, a mixture of the two acetates, $\text{HOCMe}_2\text{CH}_2\text{SAc}$ and $\text{AcOCMe}_2\text{CH}_2\text{SH}$.^{102b}

β -Hydroxypropyl mercaptan, $\text{MeCH(OH)CH}_2\text{SH}$, has been made from propylene oxide with thiourea⁵⁶ or with hydrogen sulfide. It has been obtained also from propylene chlorhydrin and sodium hydrosulfide.⁴⁹⁰ Its thioacetate, $\text{CH}_3\text{CH(OH)CH}_2\text{SCOHCH}_3$, is from propylene oxide and thioacetic acid.^{414c} The hydroxymercaptan has been prepared by catalytic hydrogenation.³³² Since the hydroxyl group is in the β -position to a sulfur atom, it is activated and can be replaced by treatment with hydrogen chloride.^{414c} Dehydration should, according to conditions, give monomeric or polymeric propylene sulfide, $(\text{CHMeCH}_2\text{S})_n$.

β -Chloropropyl mercaptan, $\text{CH}_3\text{CHClCH}_2\text{SH}$, results from the reaction of hydrogen chloride on propylene sulfide.^{102a, 431a} Acetyl chloride gives the acetate, $\text{MeCHClCH}_2\text{SCOMe}$, and acetyl bromide, the bromo compound, $\text{MeCHBrCH}_2\text{SCOMe}$.^{102a} With an acyl chloride, the propylene sulfide ring may open either way.^{431b}

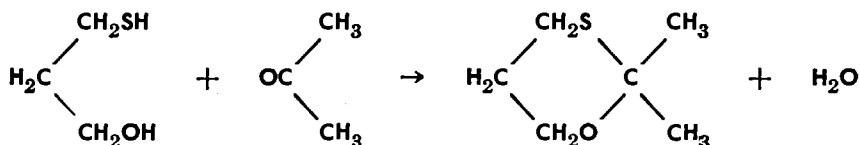
The isomeric β -mercaptopropanol-1, has been prepared by treating propylene sulfide with acetanhydride in pyridine and hydrolyzing the acetate.^{102a}

3-Mercapto-4-hydroxycoumarin has been prepared by the thiourea method.¹²¹

3-Hydroxypropyl mercaptan, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$, has been prepared from trimethylene chlorhydrin both with sodium hydrosulfide^{36, 369} and with thiourea.⁹² It appears to have been obtained by heating trimethylene sulfide with water at 200° .¹⁸¹ It is formed by the addition of hydrogen sulfide to allyl alcohol, under the influence of ultraviolet light.^{469, 470} It is produced by heating allyl alcohol, hydrogen sulfide, and hydrogen under high pressure with a sulfactive catalyst.⁶

As in this mercapto-alcohol the two reactive groups are fur-

ther apart, the one does not influence the other as much as in mercaptoethanol. With acetone, a cyclic monothioketole is formed:^{414c}



The bromide, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{SH}$, is prepared by treating the hydroxymercaptan with phosphorus tribromide.²²⁹ The chloride, $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{SH}$, is made by the addition of thioacetic acid to allyl chloride and the alcoholysis of the thiol ester.^{414b}

The ether, $\text{EtOCH}_2\text{CH}_2\text{CH}_2\text{SH}$, is from 3-ethoxypropyl bromide.³⁶⁹

γ -Hydroxybutyl mercaptan, $\text{MeCH}(\text{OH})\text{CH}_2\text{CH}_2\text{SH}$, has been obtained by the hydrogenation of aldol with a sulfactive catalyst.^{133b}

δ -Hydroxybutyl mercaptan, $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, has been prepared from 4-chlorobutanol. When passed over hot alumina, it is converted to tetrahydrothiophene.⁴⁹⁷

2-Mercapto-3-chlorobutane has been made by the addition of hydrogen sulfide to 2-chlorobutene.⁴⁶⁹

Primary alkoxy-chloropentenes react normally with alkali hydrosulfides, while with secondary there is allylic rearrangement.³⁴⁷

Cyclopentene oxide and sodium hydrosulfide give *trans* 2-mercapto-cyclopentanol.⁴⁶⁸ The *trans* thioacetate of 2-mercapto-cyclohexanol is formed by the reaction of thioacetic acid with cyclohexene oxide.^{299d}

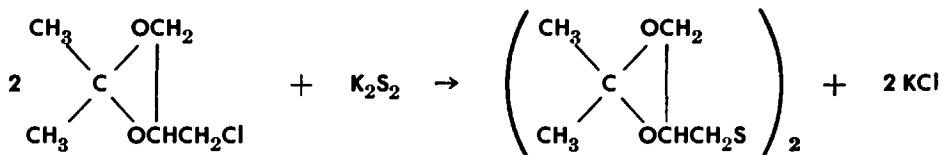
THIOGLYCEROLS



A thioglycid, apparently, $\text{CH}_2 - \text{CHCH}_2\text{SH}$, was obtained by Reboul who recognized the possibility of isomers. It gave precipitates with heavy-metal ions.³⁵⁰ Carius got mono-, di-, and tri-thioglycerols from the reaction of the mono-, di-, and tri-chlorohydrins with potassium hydrosulfide. These gave precipitates with heavy-metal ions. On heating, the first two lost water and hydrogen sulfide and the last, hydrogen sulfide. The state-

ment that the monothioglycerol was insoluble in water casts doubt on the group.^{71a}

The acetone derivative of α -chlorhydrin has been converted to the disulfide:



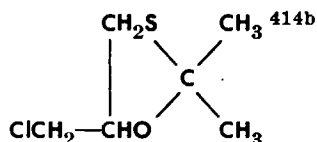
After eliminating the acetone, the disulfide was reduced to the mercaptan, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH}$.⁴¹⁶ The same compound with identical properties has been prepared by the reaction of barium hydrosulfide solution on glycid and by the hydrolysis of the reaction product of glycid with thioacetic acid.^{414c} An impure product has been obtained from monochlorhydrin.³⁰³

N-hydroxylauramide is said to react with monothioglycerol in the presence of an acid catalyst.³ An arsenic derivative has been prepared:



One part of thioglycerol in 500 of glycerol promotes the rapid healing of wounds.^{442, 443} A textile assistant has been made from it.^{424a}

Epichlorhydrin and sodium hydrosulfide, at 0° , give the chlorohydroxymercaptan, $\text{ClCH}_2\text{CH}(\text{OHCH}_2\text{SH})$, while at 50° , the product is the cyclic hydroxytrimethylene sulfide, $\text{HOCH}(\text{CH}_2)_2\text{S}$.^{414a} It is better to treat the epichlorhydrin with thioacetic acid and hydrolyze the thioacetate, $\text{AcSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$. The chlorohydroxymercaptan and acetone give the cyclic monothiomercaptole:



The formals, $\text{H}_2\text{C}(\text{SCH}_2\text{CHClCH}_2\text{Cl})_2$ and $\text{H}_2\text{C}[\text{SCH}(\text{CH}_2\text{Cl})_2]_2$, from the dichlorothiohydrins, are said to be starting materials for making polymers.^{327b} Thioepichlorhydrin and acetyl chloride give the thioacetate, $\text{ClCH}_2\text{CHClCH}_2\text{SAc}$.^{102b}

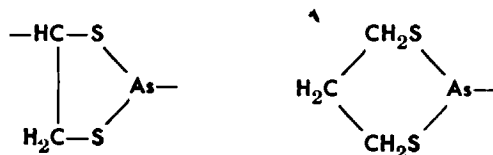
1,3-Dithioglycerol, $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH}$, has been prepared from 1,3-dichlorhydrin or 1,3-dibromohydrin, and sodium hydro-

sulfide.^{361, 413, 455} It has been obtained by the electrolytic reduction of the disulfide.^{414c} The antimony and arsenic derivatives have been reported as therapeutically active.¹⁴³

BAL

1,2-Dithioglycerol is known as BAL, which stands for British anti-lewisite. This was proposed as an antidote for lewisite, $\text{Cl}_2\text{AsCH:CHCl}$, a possible war gas. The investigation has been broadened to take in arsenic compounds in general.

It was suggested that the toxicity of arsenic to living cells might be due to its reaction with two neighboring sulfhydryl groups in an essential enzyme and that 1,2- or 1,3-dithiols might capture the arsenic by forming stable five- or six-membered rings.^{433a}



The ease of formation and stability of such rings is well known. 1,2-Dithioglycerol, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OH}$, was a likely compound with which to begin. Experiments with other metals followed those with arsenic. Other bivalent and trivalent metals seem to act like arsenic, but univalent silver does not.

1,2-Dithioglycerol can be made from dibromhydrin^{44, 105c, 303, 336, 343, 433a} or dichlorhydrin²²⁰ and sodium hydrosulfide. Many variations of solvent and of time and temperature of heating have been tried, but the yields are still only fair. It has been obtained by the hydrogenation of a polymeric trisulfide with the aid of a sulfactive cobalt catalyst.³³²

The reactions of BAL are what would be expected. It forms insoluble mercaptides with heavy-metal ions. Those with iron, lead, tin, bismuth, copper, nickel, and antimony are colored, while those with mercury, cadmium, and zinc are white.²⁶ It will take metals away from their complexes with dithizone.²²¹

Its oxidation rate has been compared with those of other dithiols. The rates depend on the distance between the two thiol groups and on the pH of the solution. It reduces methemoglobin to hemoglobin.²⁶ A tetrathionate oxidises it to the disulfide.¹⁶⁸

With an acid catalyst, it is selectively acetylated to the mono-

acetate.³³⁰ More drastic treatment gives the triacetate.¹²⁵ Heating under reduced pressure converts it to mercaptomethylethylene sulfide, with the loss of a molecule of water.^{125, 254a} In the presence of acid, it condenses with two molecules of *N*-methylolbenzamide to $\text{PhCONHCH}_2\text{SCH}_2\text{CH}(\text{SCH}_2\text{NHCOPh})\text{CH}_2\text{OH}$.⁴¹¹ It reacts with an amine and formaldehyde.²³⁴ In a solution buffered with glycine at pH 9.4, it is oxidised by air.³⁴²

The dithioglycerols are stabilized by ammonium salts and carboxamides.³⁸⁵ The selective absorptions of α -monothioglycerol and of the two dithioglycerols have been studied.^{414d}

Numerous derivatives, homologs and analogs of BAL have been synthesized in the hope of finding something more effective and less toxic. The most important of these is its glucoside, known as BAL-Intrav. Bromine is added to allyl glucoside and the resultant dibromide treated with an alkali hydrosulfide^{105a} or with potassium thioacetate.¹²⁶ To compare with this, the tri-thiogluconide has been prepared, starting with 1,2,3-propane tri-thiol.^{299c} The methyl ether, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OMe}$, the amine, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{NH}_2$, 1,3-dithioglycerol, $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH}$, and trimethylene dimercaptan are claimed in one patent³⁴³ and the methyl, ethyl, and isopropyl ethers in another.³³¹ The ether, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OCH}_2\text{CH}(\text{OMe})\text{CH}_2\text{OMe}$, has been reported.^{299a} The acetate, propionate, and butyrate of BAL have been described.³³⁰ The propionate and butyrate were among forty-three compounds tested.⁴⁶¹ Two glyceryl ethers, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, and $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OCH}(\text{CH}_2\text{OH})_2$, and an ether of glycolic acid, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}_2\text{OCH}_2\text{CO}_2\text{H}$,¹²⁶ have been reported. 2,3-Isopropylidene-dimercaptopropanol is reduced by sodium in liquid ammonia to the 2-isopropyl sulfide of BAL, $\text{HSCH}_2\text{CH}(\text{SPr-i})\text{CH}_2\text{OH}$.^{299b} As analogs of BAL-Intrav, several ethers have been made with mannitol and sorbitol derivatives.^{45b}

3,4-Dimercaptobutanol, $\text{HOCH}_2\text{CH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, has been prepared from 3,4-dibromobutanol and sodium hydrosulfide.³³⁰ It has been made also by the hydrolysis of the diacetyl derivative. The corresponding chloro compound could not be purified.^{299a} 3,4-Dimercaptobutanediol, $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}(\text{SH})\text{CH}_2\text{SH}$,^{125, 478b} and its tetraacetate have been prepared and tested against an arsenical.^{478b} Two isomers of 1,4-dimercaptobutanediol-2,3 have been prepared.¹²⁵ 1,2-Dimercaptopentanetriol-3,4,5,^{125, 498b} 1,2-di-

mercaptohexanetetrol-3,4,5,6, 1,4-dithioerythritol, and 1,6-dithiodulcitol have been described.^{498b} The ethers, $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}(\text{OMe})\text{CH}_2\text{OMe}$ and $\text{HSCH}_2\text{CH}(\text{SH})\text{CH}(\text{OMe})\text{CH}(\text{OMe})\text{CH}_2\text{OMe}$, have been prepared.^{299a} Dithiopentaerythritol, $(\text{HSCH}_2)_2\text{C}(\text{CH}_2\text{OH})_2$, has been made in three ways: by the catalytic hydrogenation of the disulfide,³³² by the reduction of the disulfide,¹³ and by hydrolysis of the dithioacetate, $(\text{AcSCH}_2)_2\text{C}(\text{CH}_2\text{O})_2\text{CMe}_2$.^{45a} 1,6-Dithiomannitol, $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{SH}$, has been reported.^{45a, 125} The dibromides of 5,6-sorbitoleen and 1,2-mannitoleen have been the starting materials for preparing dithiohexitols.^{45c}

Pharmacology of BAL

A number of reviews have been devoted, in whole or in part, to BAL.^{8, 70, 176, 183, 241, 268, 335, 346, 348, 368, 456, 480, 491} The development of the antidotes for lewisite has been reviewed.^{334, 476} Experiments on five thousand men using forty-three compounds have been reported.⁴⁶¹ Comparisons have been made with other dithiols.^{79, 138, 496} BAL protects against lewisite in the eyes,^{194, 210, 293} on the skin¹⁷⁵ and in the lungs.¹⁹⁵ It protects living cells in vitro.¹³⁷ It reverses the enzyme inhibition caused by lewisite²⁵ and is effective against arsenic compounds in general.^{15, 48, 72, 81a, 115, 116, 118, 123, 165, 180, 269, 271, 277, 366, 367, 430, 434b, 435, 436, 439, 463, 491} The excretion of arsenic is increased.^{74, 273, 485} A compound from oxophenarsine and BAL is said to combine low toxicity with significant trypanocidal and spirochetocidal activity.^{144, 380, 478b} An antimony derivative is recommended for schistosomiasis.⁸⁷

BAL counteracts the toxic action of mercurials.^{24, 29, 33, 60, 81b, 119, 120, 129, 165, 188, 238, 239, 247, 264, 267, 269, 270, 333, 433b, 440, 462} It is effective against compounds of lead,^{84, 162, 173, 177, 277, 279, 376, 453, 478a} cadmium,^{24, 167, 193, 454, 464} antimony,^{60, 117, 143, 154, 430, 462} copper,²⁷⁷ bismuth,^{24, 60, 430} nickel,⁶⁰ arsenic,¹⁴³ chromium,⁶⁰ gold,^{47, 164, 246, 263, 294, 430, 462} tungsten,²⁷⁷ and tellurium,⁷ but not against those of silver,^{161, 317} uranium,^{277, 287b, 288, 310} or selenium.³² It increases the excretion of copper enormously.^{282, 286} BAL is therapeutically active in propylene glycol solution.¹⁴³ Water-soluble derivatives are said to be effective and less toxic.⁶⁴

The physiological effects have been the subject of numerous studies some of which are listed.^{16, 17, 27, 38, 39, 67, 73, 80, 86, 95, 103,}

104, 106, 110, 128, 155, 207, 253, 278, 295, 322, 337, 342, 351, 362, 378, 434a, 457, 459, 479, 486 The toxicology of BAL has been investigated extensively.^{78, 105b, 114, 196, 204, 212, 245, 287a, 375, 426b} Its metabolism has been studied⁴²⁷ and has been followed by means of S^{35} .³³⁴ Its toxicity to various animals has been determined.^{99, 100, 226, 233, 285, 301, 302, 438}

The investigation of the pharmacology of BAL glucoside has gone along with that of BAL itself.^{99, 100, 166, 167, 454, 478a, 478b}

Two colorimetric methods for estimating BAL have been proposed, depending on the reaction with cyanogen chloride⁵ or with cobalt nitrate.^{426a} A manometric method is based on the amount of nitrogen evolved with iodine and sodium azide.²²²

1-THIOSORBITOL

This is readily prepared by heating an aqueous solution of glucose with a catalyst, sulfur and hydrogen under 1000 lb. pressure at 150° for several hours. The crude product may be purified by recrystallization from ethanol. A purer product is obtained by decomposing the cuprous salt in water with hydrogen sulfide or by hydrogenolysis of the disulfide.^{132, 133a, 133b, 254b, 332}

1-Thiosorbitol is a white crystalline solid, melting at 93° and very soluble in water, less so in alcohol. It has the characteristic reactions of polyhydric alcohols and of mercaptans. The hexaacetate can be prepared in the usual way. In alkaline solution it reacts with an alkyl halide to form a sulfide. Like any other mercaptan it forms salts with heavy-metal ions, such as cuprous, cupric, ferrous, mercuric, lead, stannous, nickel and zinc. The remarkable thing about these mercaptides is that they are soluble in water. The best way to make them is to dissolve the freshly precipitated metal hydroxide in an aqueous solution of the mercaptan.^{410b} Thiosorbitol dissolves silver chloride with the liberation of hydrochloric acid.

Thiosorbitol has attracted considerable attention. It is a strong reducing agent.¹⁶⁸ It should duplicate many of the reactions of mercaptoethanol since it has a hydroxyl group on the carbon next to the one that carries the sulfhydryl. This hydroxyl should be labile. A molecule of water should be formed by removing it along with a hydrogen from a sulfhydryl group. The result would be either a cyclic sulfide or a linear polymer.

Thiosorbitol has been recommended as a stabilizer for poly-

vinyl chloride and the like,¹¹² as an anticorrosion agent for pickling baths⁵⁵ and as a constituent for plating baths.⁴¹²

The pharmacology has been studied extensively.^{160, 166, 167, 196, 404} The gold derivative has been used in arthritis.³⁰⁴

AROMATIC HYDROXY MERCAPTANS

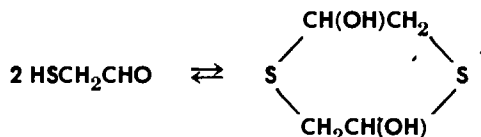
These can be prepared by the methods used for the unsubstituted mercaptans. Sulfonyl chlorides may be reduced by zinc and acid.^{158, 163, 230, 290, 341, 446, 465, 498, 499} The free phenol group is usually protected by converting it to the ethyl carbonate. An aromatic aminomercaptan³⁵⁵ or an aminophenol⁴⁷⁷ can be changed to the mercaptophenol by the diazo reaction. A disulfide may be reduced.^{59, 355} In *p*-chlorophenol, the chlorine may be replaced by a sulfhydryl group by heating with sodium sulfide and hydroxide.^{217a, 219a, 323a} A peculiar method is the treatment of sodium phenate with a mixture of sodium sulfide and disulfide.^{217b, 219b, 323b}

The ozonization of thionaphthene gives hydroxythiophenols which go into disulfides.⁴⁷⁴ Pentachlorothiophenol has been made by coupling the appropriate diazonium chloride with potassium xanthate and hydrolyzing.⁴⁴⁸ Dithiogalein is made by heating fluorescein with sulfur.³⁰⁷ Alkylmercaptoquinones are reduced to the corresponding hydroquinones by zinc and acid.⁴ Hydroxy- and alkoxy-benzyl mercaptans can be made by the thiourea method.²⁶⁵

The acidity potentials of several hydroxythiophenols have been measured.⁴⁰⁵

Aldehydo-Mercaptans

Benzylmercaptoacetal, $\text{PhCH}_2\text{SCH}_2\text{CH}(\text{OEt})_2$, is split by sodium in liquid ammonia. The resulting mercaptoacetal is hydrolyzed to the mercaptan which is in equilibrium with its dimer:



This synthesis was carried out to identify the aldehyde, $\text{C}_2\text{H}_3\text{-OSH}$, which had been obtained by the hydrolysis of uscharin.^{201, 202} The mercaptoacetal has been obtained also from bromoacetal

and potassium hydrosulfide.^{182, 325} This will be treated again under cyclic sulfides.

The addition of thioacetic acid to acrolein gives β -acetylmercaptopropionaldehyde, $\text{MeCOSCH}_2\text{CH}_2\text{CHO}$, b_{11} 89° ; $n_{25/D}$ 1.4887. Similar compounds are obtained from methacrolein and from 2-ethylhexenal⁴⁷² but the mercaptoaldehydes have not been isolated from these.

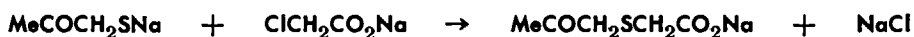
o-Mercaptobenzaldehyde has been prepared, but little is known about it. It can be degraded to *o*-hydroxythiophenol by the decomposition of an ozonide.⁴⁷³

Keto-Mercaptans

Chloroacetone reacts regularly with sodium hydrosulfide:^{208, 225, 316, 338, 403}



The product exists in two, probably polymeric, forms, $m.80-2^\circ$ and $109-11^\circ$. It is dimeric in bromoform. As a ketone, it forms an oxime and as a mercaptan, it reacts with chloroacetic acid, in alkaline solution:⁴⁰³



By loss of water, the dimer passes into 2,5-dimethyl-2,5-endoxydithiane.²⁰⁸ This will be discussed again under cyclic sulfides. Similarly, 1-mercapto-2-octanone, $\text{HSCH}_2\text{COC}_6\text{H}_{13}$, has been prepared.²²⁵

The addition of hydrogen sulfide to mesityl oxide gives 2-methyl-2-mercaptopentanone-4, $\text{Me}_2\text{C}(\text{SH})\text{CH}_2\text{COMe}$.^{9, 139} Adding thioacetic acid to 2-methyl-2-octenone-7 and hydrolyzing the product yields 2-methyl-3-mercapto-octanone-7.²⁸

s-Dimercaptoacetone, $\text{HSCH}_2\text{COCH}_2\text{SH}$, has been prepared from *s*-dichloroacetone and sodium hydrosulfide.^{338, 403}

Phenacyl mercaptan, PhCOCH_2SH , has been obtained from phenacyl bromide and sodium hydrosulfide.¹⁸⁴ It is better to prepare it from phenacyl chloride and sodium thiosulfate.^{20, 244} It is an unstable yellow oil which has been characterized only by its derivatives. *m*-Nitrophenacyl, β -naphthacyl, α -methylphenacyl, and desyl mercaptans have been made from the thiosulfate, but only as intermediates.²⁰ The desyl has been isolated.⁴⁰² *p*-Phenyl-

phenacyl mercaptan has been obtained from the sulfonium bromide and hydrogen sulfide.⁵⁷

The dimercaptan, ArCOCH:C(SH)_2 , is formed when an aryl methyl ketone is treated with carbon disulfide and alkali. The product first formed is probably the salt of the dithioacid, $\text{ArCOCH}_2\text{CSSK}$, but it alkylates to the alkyl derivative, ArCOCH:C(SR)_2 . A number of these have been prepared.^{231, 232} This will be treated again in a later chapter.

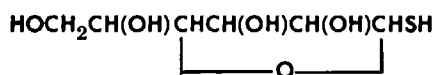
o-Mercaptoacetophenone, $\text{HSC}_6\text{H}_4\text{COCH}_3$, has been obtained as one of the hydrolysis products of 1-acetyl-2-methylene-1,2-dihydrobenzisothiazole. It has been characterized only through its derivatives.²⁸³ The meta⁴⁰⁶ and para^{364, 406} isomers have been prepared from the diazonium salts and xanthate. The para has been made also by decomposing β -(*p*-acetylphenylthio)- β -(*m*-nitrophenyl)-propiophenone with lead hydroxide.²⁰⁰ 3,5-Dimercaptoacetophenone and 2,4-dimercaptoacetophenone have been obtained by reducing the corresponding disulfonyl chlorides.³⁶⁴ β -Mercaptoanthraquinone¹⁴⁶ and 4,4'-dimercaptobenzophenone⁴⁴⁸ have been prepared by the diazonium-xanthate method. The acetylation of a 3-alkylthiophenol gives a 2-acetyl-5-alkylthiophenyl acetate which is hydrolyzed to a 2-acetyl-5-alkylthiophenol.¹³⁰ Some α -ketothiols lose hydrogen sulfide easily. Thiobenzoin gives desoxybenzoin with sulfuric acid.²²³

Thiosaccharides

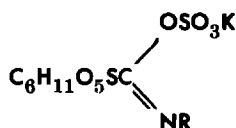
There are two groups, the thioglycoses, or true mercaptans, in which a primary or secondary -OH is replaced by an -SH , and the glycothioses in which a sulfur atom takes the place of the aldehyde oxygen. Strictly speaking these are hemithials and should be in the chapter on thiones and thials. However, they are prepared by the methods by which thiols are made and their reactions are typical mercaptan reactions.

THIOSES

The one important member of this group is β -thioglucose which has the structure:



There is some uncertainty whether it is a furanose or a pyranose. It is the characteristic constituent of several glucosides which are found in natural products. The history of this group goes back to the isolation in 1825 of a crystalline compound containing nitrogen and sulfur from white mustard seed.¹⁹⁹ Five of these thioglucosides have the structure:



Hydrolysis may split at one side or the other of the sulfur atom so as to give glucose and an isothiocyanate, SCNR, or thioglucose. Potassium bisulfate is formed in either case. In sinigrin, the R is allyl,^{58, 69, 134, 153a, 388b, 393, 399, 488} in glucotropacolin, benzyl,²⁰⁶ in gluconasturtin,^{153b, 206} β -phenylethyl, and in glucocheirolin, methyl α -propyl sulfone, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{CH}_3$.^{388a, 396, 397, 475} The breakdown of sinigrin into glucose and allyl isothiocyanate, known as mustard oil, is taken up under thiocyanates. Sinalbin is more complicated. The R is *p*-hydroxybenzyl and instead of the potassium, there is the choline ester of 3,5-dimethoxy-4-hydroxycinnamic acid, $\text{HO}(\text{MeO})_2\text{C}_6\text{H}_2\text{CH}:\text{CHCO}_2\text{CH}_2\text{CH}_2\text{N}(\text{Me})_3\text{OH}$.^{10, 58, 153b, 489} Thioglucose is formed from all of these by the action of ammoniacal silver solutions.

The chemistry of sinalbin and thioglucose has been summed up by Specht⁴²⁵ and the subject has been brought up to date by Raymond.³⁴⁹

Synthesis of Glucothiose

Tetraacetobromoglucose reacts smoothly with potassium xanthate, KSCSOEt . Acid hydrolysis splits off the xanthate group, but leaves the acetyls. Ammonia in methanol removes these also, leaving the glucothiose.³⁹⁴ Acetylated bromoglucose and potassium disulfide gave the disulfide which was reduced by zinc and acetic acid to the desired thioglucose.^{493a} This reduces Fehling's solution in the cold and forms a phenylglucosazone with phenylhydrazine. The thiol is eliminated in this reaction as it should be. It shows the normal mutarotation. It yields a crystalline pentaacetate and may be oxidised by iodine to the disulfide.^{363, 387, 395, 407} Another method of synthesis involves the reaction of

tetraacetylglucose with potassium thioacetate, MeCOSK. The resulting pentaacetate is deacetylated.^{141, 381a} The synthetic and the natural have been compared in several ways and found to be identical,⁴⁹⁴ except that they have opposite rotations.^{493b} Thioglucose has been prepared also through the phenyl thiourethane-D-glucoside.^{391, 392}

Tetraacetyl-D-glucoside-S-thiuronium bromide and sodium nitrite give octaacetyl- β,β -diglucosyl sulfoxide-sulfide, $\text{Ac}_4\text{C}_6\text{H}_7\text{O}_5\text{-SO-SC}_6\text{H}_7\text{O}_5\text{Ac}_4$.³⁸⁹

In addition to glucothiose, cellothiose,⁴⁹⁵ xylothiose,¹⁵⁹ and a trithiogalactose³⁹⁰ have been synthesized.

When glucose, dissolved in dry pyridine, is saturated with hydrogen sulfide, thioglucose is formed along with some dithio compound. Similar results were obtained with D-mannose, D-fructose, L-rhamnose, L-arabinose, lactose, and maltose.^{388c, 398}

The reactivities⁴¹⁸ and photochemical properties²⁴³ of thioglucose have been compared to those of other mercapto-compounds. The rates of its reactions with iodoacetamide and with iodoacetate have been measured.⁴¹⁸

Thioglucose stimulates cell proliferation in mammals as in lower organisms.¹⁸⁷ Dressings of thioglucose aid in healing ulcerated areas.³⁵⁴ It stabilizes ascorbic acid.³²⁰ There has been considerable interest in therapeutic uses of the gold derivative, the production of which has been described.^{77, 381c, 385, 400} It is highly bactericidal.³³⁹ Its toxicity has been studied.¹⁰⁹ One injection of it causes gain in adipose tissue in albino mice.⁶¹ It affects the liver function in dogs.¹⁸⁵ Its complex with sodium thiosulfate is said to be effective against infections.³⁸² The distribution of gold in various organs of the body, after dosage with aurothioglucose has been determined.^{46, 111, 275, 340} It is eliminated largely in the urine.⁴⁶ Bismuth,^{77, 381c, 400} cadmium,^{77, 400} and sodium thioglucose^{381b} have been advocated as therapeutic agents, so have the silver-sodium,³⁸⁶ antimony-sodium³⁸⁴ and antimony-silver^{381c} double salts. The gold derivative of thiocellulose^{381c} and the silver and mercury derivatives of cellobiose have been claimed as medicinals.^{493c} Thioglucose, thiogalactose, and thio-cellobiose increase the physiological activity of gold glutathionate.¹³⁶

Adenyl (mercaptomethyl) pentose contains 9'-(5-mercaptomethyl) pentose.³⁷⁹

THIOGLYCOSES

Little is known of the thioglycoses in which a hydroxyl is replaced by a sulfhydryl group. The S-methyl derivative of one of these, which is found in yeast, will be treated in the chapter on substituted sulfides as a hydroxy-sulfide.

Acetone-6-thio-D-glucose has been made by saturating an aqueous barium hydroxide solution of 5,6-anhydroacetonefructose with hydrogen sulfide. The 6-thioglucofuranose has not been obtained in crystalline form and has not been well characterized.³¹⁵

3-Thioglucofuranose has been obtained from the rearranged xanthate of diacetoneglucose. The 3-thioglucofuranose did not crystallize, but yielded a crystalline tetraacetate and disulfide.¹⁴²

Sulfide-Mercaptans

The sulfide-mercaptans, $RS(CH_2)_nSH$, in general, can be made by the standard methods for preparing mercaptans. The only special cases are where $n = 1$, or 2. The compounds in which $n = 1$, $RSCH_2SH$, are hemimercaptals and unstable. The ethyl compound, $EtSCH_2SH$, has been obtained by the reaction of the chloride with dry potassium hydrosulfide at -4° .⁵¹ When hydrogen sulfide is passed into a cold neutral solution of formaldehyde, an unstable heavy liquid separates out. This appears to contain $HSCH_2SH$, $HSCH_2SCH_2SH$ and $HSCH_2SCH_2SCH_2SH$. These cannot be isolated, but their methyl derivatives, $MeSCH_2SMe$ and $MeSCH_2SCH_2SMe$, have been obtained and oxidised to the corresponding sulfones.³⁰

The compounds, $RSCH_2CH_2SH$, in which $n = 2$, are by far the best known, since they can be prepared from the chlorides, $RSCH_2CH_2Cl$. As will be shown in the chapter on substituted sulfides, many of these chlorides have been made for toxicity studies. The mercaptan, $EtSCH_2CH_2SH$, is readily obtained from the chloride, $EtSCH_2CH_2Cl$.^{108, 174} It turns out that this mercaptan can be made directly from the alcohol, $EtSCH_2CH_2OH$, which saves the trouble of converting it to the chloride.³⁵² It is known that mercaptans can be obtained from other alcohols in this way, but long heating and high concentrations of acid are

required unless the hydroxyl is activated as it is by the β -sulfur atom. A special method is the reaction of ethylene sulfide with a mercaptan:^{297, 358}

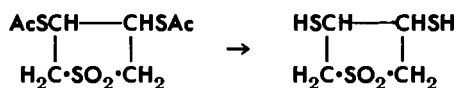


This is analogous to the reaction of ethylene oxide with an alcohol. *i*-Butylene sulfide and a mercaptan give two products, $\text{RSCMe}_2\text{CH}_2\text{SH}$ and $\text{RSCH}_2\text{CMe}_2\text{SH}$.^{422b} Ethylene is sulfurized and hydrogenated in the presence of cobalt trisulfide under pressure at 170 to 250°. One of the products is $\text{EtSCH}_2\text{CH}_2\text{SH}$.^{255, 410a}

The sulfide-dimercaptan, $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$, is a by-product in the preparation of ethylene mercaptan.^{296, 298} The bis-sulfidedimercaptan, $\text{HSCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$, is also a by-product.²⁹⁸ The sulfide-dimercaptan can be prepared from dichloroethyl sulfide and thiourea in the usual way.¹⁹¹ The formation of the isothiuronium salt is rapid when the mixture of the reactants and water is heated under reflux. It is complete within 30 minutes. The yield of distilled product is 81%. An equally good yield is obtained directly from thiodiglycol. A mixture of 122 g. thiodiglycol (1 mole), 155 g. thiourea (2.04 moles), and 200 cc. of concentrated hydrochloric acid (2.35 moles) is heated under reflux. The formation of the isothiuronium salt is complete within 20 minutes. It is known that concentrated hydrochloric acid reacts rapidly with thiodiglycol to form the chloride and it is possible that the chloride is an intermediate, but its presence has not been observed. However, the preparation should be made under a hood. The advantage of this method is that it obviates handling the toxic dichloride. This sulfide-dimercaptan forms a red nickel complex which is a sensitive test for mustard gas.¹⁹¹

This method has been applied to the higher glycols $(\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2$, $(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2$, $\text{CH}_2(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2$ and $\text{O}_2\text{S}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH})_2$. In all of these, the hydroxyls are in β -positions to sulfur atoms.³⁵²

The sulfide-dimercaptan, $\text{S}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_2$, is a by-product in the preparation of trimethylene mercaptan.²⁹⁸ From the bromine addition product of butadiene sulfone and thioacetic acid in pyridine, a bisthioacetate has been obtained. This can be deacetylated to the dimercaptan:³²⁹



The aromatic sulfide-dimercaptan, *p,p'*-HSC₆H₄SC₆H₄SH, has been prepared.³⁴⁸

Aminomercaptans

FORMATION

The simplest aminomercaptan, H₂NCH₂SH, like its analogs, HOCH₂OH and HOCH₂SH, is unstable and has never been isolated, but certain of its derivatives are known. The grouping, -N:C(SH)-, is present in 2-mercaptopyridine⁴⁵⁸ and in 2-mercaptoquinoline.³⁷⁰ Treating piperidine and morpholine with formaldehyde and then with hydrogen sulfide gives the compounds, CH₂(CH₂CH₂)₂NCH₂SH and O(CH₂CH₂)₂NCH₂SH.⁴² These are also made by treating the 2-hydroxy compounds with phosphorus pentasulfide. The urea derivative, OC(NHCH₂SH)₂, is said to improve the resistance of wool to alkali.¹¹³ 5-Alkyl-4-alkylamino-2-pyrimidinethiols have been prepared by heating 5-alkyl-2,4-dithiouracils with an amine. This is true also of the corresponding 5-aryls and of the unsubstituted forms.^{68, 481} 4-Phenyl-5-imidazolethiol contains both HS·C·N and HS·C·C·N groupings.¹

Aminomercaptans, in which the amino and sulfhydryl groups are on different carbon atoms, can be synthesized by the usual methods for mercaptans.

Potassium phthalimide and an excess of ethylene bromide give the bromide, C₆H₄(CO)₂NCH₂CH₂Br, which can be treated with an alkali hydrosulfide, xanthate, or thiourea and the product hydrolyzed to β-aminoethyl mercaptan, H₂NCH₂CH₂SH.^{92, 149a, 150, 151, 306, 415} β-Aminopropyl mercaptan has been prepared in this way.⁴⁰⁸

β-Aminoethyl mercaptan is of special interest, since the amide of pantothenic acid, RCONHCH₂CH₂SH, a constituent of coenzyme-A, is derived from it.^{18, 178, 179, 280, 281, 419} The S-acetyl derivative of this amide is potent pharmacologically. This amide can be obtained from pantothenic acid in several ways.^{326, 420} An amide of this type can be prepared by treating a thioacid with ethylene imine.¹⁹ The pK_a value for S-acetoacetyl-N-acylthio-

ethanolamine is 8.5, compared to 10.7 for ethyl acetoacetate.⁴⁸³ The N-(mercaptoethyl)amide, $\text{PhCOCMe}_2\text{CONHCH}_2\text{CH}_2\text{SH}$, has been made from the β -lactam.²¹

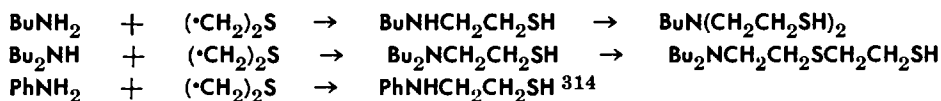
Dialkylaminoalkyl halides, $\text{R}_2\text{N}(\text{CH}_2)_n\text{Cl}$, can be used directly for the synthesis of mercaptans. Of these the chlorides, $\text{R}_2\text{NCH}_2\text{CH}_2\text{Cl}$, are the most available and thus those most often employed. These react regularly with an alkali hydrosulfide^{171, 452} or with thiourea.^{2, 89, 90, 91, 172, 444} The higher homologs, where $n > 2$, react similarly.^{89, 91, 250} The result is the preparation of many dialkylaminomercaptans, $\text{R}_2\text{N}(\text{CH}_2)_n\text{SH}$. Methyl-di(mercaptoethyl)amine, $\text{MeN}(\text{CH}_2\text{CH}_2\text{SH})_2$, ethyl-di(mercaptoethyl)-amine, and tri(mercaptoethyl)amine, $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$, have been prepared. The colored compounds, which these give with nickel, provide a sensitive test for the nitrogen mustards.¹⁹¹

Thiocholine chloride, $\text{HSCH}_2\text{CH}_2\text{NMe}_3\text{Cl}$, has been made by heating the chloride, $\text{ClCH}_2\text{CH}_2\text{NMe}_3\text{Cl}$, with thiouracil.¹⁹⁰ The acetyl derivatives of thiocholine and of β -methylthiocholine have been prepared, starting with $\text{ClCH}_2\text{CH}_2\text{NMe}_2$ and $\text{ClCHMeCH}_2\text{NMe}_2$, which react with thiourea.³⁵⁷ The iodide, $\text{AcSCH}_2\text{CH}_2\text{NMe}_3\text{I}$, is from the addition of trimethylamine to acetylmercaptoethyl iodide.²²⁴

A novel method is the treatment of lithium diethylamine with ethylene sulfide:¹⁷²



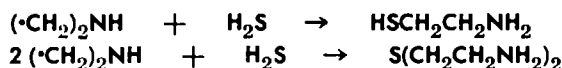
Without the lithium the diethylamine has to be heated with the ethylene sulfide in a sealed tube. Ethylene and propylene sulfide react with primary and secondary amines: 213d, 216, 359, 421b, 421c, 422a



Isobutylene sulfide and piperidine give $\text{C}_5\text{H}_{10}\text{NCH}_2\text{CMe}_2\text{SH}$. These reactions are analogous to those of amines with ethylene oxide. Trimethylene sulfide reacts similarly:¹⁸¹

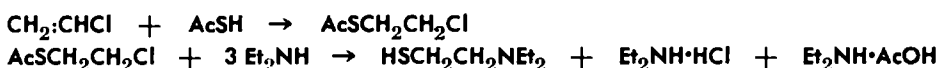


Ethylene imine reacts with hydrogen sulfide even at -60° : 23, 41, 300, 308

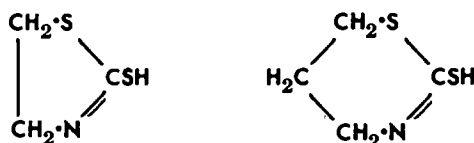


An excess of hydrogen sulfide favors the mercaptan.⁴⁰ An alkylene imine gives a 2-mercaptoamine, $\text{RCH}(\text{SH})\text{CH}_2\text{NH}_2$.⁵⁴

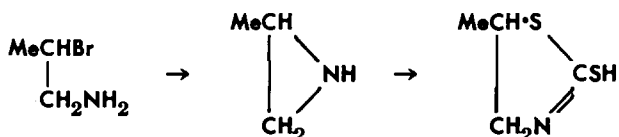
The amino and mercapto groups may be introduced in the reverse order:¹³¹



Carbon disulfide reacts with 2-aminoethyl bromide and with 3-aminopropyl bromide to give 2-mercaptothiazoline^{149a, 152, 252} and 2-mercaptopentthiazoline:²⁵²



The hydrolysis of these gives 2-aminoethyl and 3-aminopropyl mercaptans.^{152, 252} The 2-aminoethyl mercaptan may also be obtained by the catalytic hydrogenation of the 2-mercaptothiazoline.^{254c} The cyclic imine may be an intermediate in the formation of the thiazoline:⁵²



β -Aminomercaptans are conveniently made by the hydrolysis of thiazolidines.^{149a, 152, 213a, 215b, 300, 308}

Aromatic aminomercaptans have been obtained by the reduction of the appropriate sulfone chlorides.^{429, 450, 500, 501, 503} Ortho and para thiocyananiline, $\text{H}_2\text{NC}_6\text{H}_4\text{SCN}$,^{213b, 215a, 292} and nitrodisulfides^{22, 53, 135, 205b} are reduced to aminothiophenols. Sodium sulfide replaces the chlorine and reduces the nitro group of *p*-nitrochlorobenzene.¹⁷⁰ 2-Chloro-5-nitroaniline^{205a} and 2-bromo-5-nitroaniline¹⁴⁵ are converted to 2-amino-4-nitrothiophenol by sodium sulfide and sulfur. Some sulfide is also formed.

The most practical way to make *o*-aminothiophenol is the hydrolysis of benzothiazole. Substituents in the benzene ring remain, while those in the 2-position are eliminated.^{93, 156, 218c, 218, 237, 428, 437} A substituent in the 3-position stays on the nitro-

gen.^{158, 159} The catalytic hydrogenation of 2-mercaptobenzothiazole gives *o*-aminothiophenol.^{254c} Hydrolysis accomplishes the same end. 2-Amino-4-chlorothiophenol was prepared from the benzothiazole²⁴⁸ and its diacyl derivatives studied.^{248, 249}

4-Dimethylaminophenyl lithium reacts with sulfur:



Hydrolysis of this gives the amino-mercaptan, $\text{Me}_2\text{NC}_6\text{H}_4\text{SH}$.¹⁶⁹

Several mercaptoalkyl pyridines have been prepared from the corresponding chloroalkylpyridines by standard methods.^{88, 471} A halogen atom in the 2-position in pyridine is replaced readily.^{242, 458} 2-Mercapto-5-nitropyridine has been obtained in two isomeric forms, one brown, m.190°, the other yellow, m.185°. ⁴⁴⁹ 2-Mercapto-3,5-diiodopyridine is formed when 3,5-diiodopyridone is treated with phosphorus pentasulfide.²⁴⁰

REACTIONS

The fact that β -aminoethyl mercaptan is a solid, with a comparatively high melting point, indicates that it exists as an inner salt.¹⁵⁰ The same can be said of many of the amino-mercaptans.

In general, there are two sets of reactions, those characteristic of amines and those of mercaptans. Naturally, the activity of each group is modified somewhat by the presence of the other. When the amino group is in the beta- or gamma-position to the sulfhydryl group, the two are frequently involved in ring formation.^{53, 93, 98, 149a, 149b, 152, 227, 300} Diethylaminoethyl mercaptan adds to acrylonitrile: ⁹²



β -Aminoethyl mercaptan forms mercaptides, two of which will be mentioned: $\text{EtHgSCH}_2\text{CH}_2\text{NMe}_2$, which quarternizes with dimethyl sulfate to $\text{EtHgSCH}_2\text{CH}_2\text{NMe}_3\text{SO}_4\text{Me}$,⁸⁵ and $\text{Et}_2\text{AuSCH}_2\text{CH}_2\text{NH}_2$, an electrolyte, which forms complexes with ethylmercaptoethyl amine and with thiourea.¹²⁷

The S-acetyl derivative is formed when the hydrochloride is treated with acetyl chloride.^{18, 487} In pyridine, the diacetyl derivative is formed.^{18, 197}

o-Aminophenyl mercaptides of copper, zinc, bismuth, mercury, cadmium,⁷⁶ cobalt, and nickel ^{76, 203} have been described.

o-Aminothiophenol and cyanogen give 2,2'-bibenzothiazolyl.²⁰⁸

APPLICATIONS

2,3-Dimercaptopropyl amine is said to be a good antidote against arsenicals.^{336, 348, 433a, 461} Thio esters of aminomercaptans are of pharmacological interest.^{89, 90} Diethylaminoethyl *p*-aminothiobenzoate, $\text{H}_2\text{NC}_6\text{H}_4\text{COSCH}_2\text{CH}_2\text{NEt}_2$, "thiocain" has been tested as a local anesthetic.^{2, 140, 192, 289, 311} Injection of β -aminoethyl mercaptan, or its salts, is said to protect humans for 2 to 3 days against ionic radiations.⁴²³ N-(β -phenylacetylmercaptoethyl)phenyl acetamide and β -phenylacetyl aminoethyl disulfide have been suggested as precursors of penicillin.³¹ Thioacetylcholine has been compared to acetylcholine.³⁵⁷

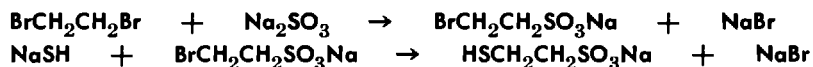
Aminomercaptans are claimed as intermediates for dyes and vulcanization accelerators.^{213c, 359} 1,3-Dimercapto-2-methyl-2-aminopropane is said to be useful in reclaiming rubber.¹⁰¹ Water-soluble salts of aminomercaptans, in which the nitrogen is tertiary, are claimed as bactericides.²¹⁴

Mercapto-Sulfonic Acids

A methane trisulfonic acid, $\text{HSC}(\text{SO}_3\text{H})_3$, has been discussed in Chapter 3.

The chief interest in these acids has been in the use of their gold, antimony, bismuth, silver and mercury derivatives as therapeutic agents. The mercaptides of these metals are solubilized by the sulfonic salt at the other end.

Ethylene bromide may react with sodium sulfite and then with a hydrosulfide: ²⁶⁶



The silver-sodium, $\text{AgSCH}_2\text{CH}_2\text{SO}_3\text{Na}$,^{275, 276a} and the gold-calcium, $(\text{AuSCH}_2\text{CH}_2\text{SO}_3)_2\text{Ca}$,^{257b} salts have been recommended. Similar compounds have been prepared, starting with trimethylene bromide.²⁶⁶ The amounts of gold deposited in various organs have been determined.³⁴⁰ Derivatives of the 3-mercapto-2-hydroxysulfonic acid, $\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{H}$, have been extensively studied. Among these are $\text{AuSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Na}$,^{262, 276b} $[\text{AuSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3]_2\text{Sr}$,^{257a, 258} $\text{Sb}[\text{SCH}_2\text{CH}(\text{OH})\text{SO}_3\text{Na}]_3$,^{260, 274b, 373} $\text{AgSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Na}$,^{274a} $\text{Bi}[\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Na}]_3$,²⁵⁹ and $\text{Hg}[\text{SCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Na}]_2$.²⁶¹

Derivatives of β -amino- α -mercaptoethanesulfonic acids, $\text{RNH-CH}_2\text{CH(SH)SO}_3\text{H}$, and their mercaptan salts have been claimed.^{383, 401} The sodium salt of the N-methylol-lauramide condensation product with 2-mercaptoethanesulfonic acid has been patented.^{424b}

Physical Properties

The physical properties of a number of compounds of this group will be listed. The object is to show what compounds have been made and, by means of the references, to tell who made them. The remarks made in Chapter 1 as to the sketchiness of the published data apply here with equal force.

HYDROXY-MERCAPTANS

HOCH_2SH , Ac., b_{14} 62–3°.⁵⁰

$\text{HOCH}_2\text{CH}_2\text{SH}$, b_{12} 54°, ⁸³ b_{13} 55°, ^{34b} b_{17} 65°, ⁷⁵ b_{18} 58°, ^{34a} b_{19} 61°, ¹⁴⁷ b_{22} 62–7°, ³³² b_{742} 157–8°; d 0/4 1.1317, d 10/4 1.1230, d 20/4 1.1143, ^{34b} 1.1153; n 20/D 1.4443, ^{34a} 1.4996; ^{34b} Ac., b_1 95°; Bz., b_1 134°; d 20/4 1.209; n 20/D 1.594; ³¹³ diBz., m.39°; ¹⁴⁷ diAc., b_{11} 98–9°.¹⁴⁸

$\text{HOCHMeCH}_2\text{SH}$, b_8 45°, ⁴⁹⁰ b_{12} 51°, ^{414c} b_{14} 55–7°, ⁵⁶ b_{20} 72°, ^{102a} d 20/4 1.0483; ^{414c} n 16/D 1.4815, ^{102a} n 18/D 1.4850, ⁴⁹⁰ n 20/D 1.4862; ^{324, 414c} diAc., b_{19} 124°; n 20/D 1.467.^{102a}

$\text{HOCH}_2\text{CHMeSH}$, b_{20} 62°; n 17/D 1.4818; diAc., b_{11} 105°; n 17/D 1.4702.^{102a}

$\text{HOCMe}_2\text{CH}_2\text{SH}$, b_{26} 64°; n 25/D 1.4768.³²⁴

$\text{HOCH}_2\text{CMe}_2\text{SH}$, b_{30} 70°; n 22/D 1.469; diAc., b_{15} 114°.^{102b}

$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_7 75–80°, ⁹² b_{10} 82°, ²²⁹ b_{15} 85–90°; ³⁶⁹ diAc., b_{15} 118–20°, ³⁶⁹ b_{24} 125°; n 20/D 1.4720; SAc., $b_{1.5}$ 72–5°; n 20/D 1.4827.⁶⁵

$\text{HOCH}_2\text{CH}_2\text{CHMeSAc}$, b_{15} 85°; n 20/D 1.4605; Ac., b_{11} 110°; n 20/D 1.4674.⁶⁵

$\text{HOCH}_2\text{CHMeCH}_2\text{SAc}$, b_{23} 121–2°; n 20/D 1.4856; Ac., b_{24} 133–4°; n 20/D 1.4693.⁶⁵

$\text{HOCH}_2\text{CH}_2\text{CHPhSAc}$, Ac., b_1 124–30°; n 20/D 1.5292.⁶⁵

$\text{HOCH}_2\text{CH(OH)CH}_2\text{SH}$, $b_{0.9}$ 95–7°, b_1 101°, ^{414c} b_3 112°; ⁴¹⁶ d 20/4 1.2455; n 20/D 1.5268; ^{414c, 416} triAc., $b_{1.8}$ 130–6°.^{414c}

$\text{HSCH}_2\text{CH(OH)CH}_2\text{SH}$, $b_{0.04}$ 55°, ⁴¹³ $b_{1.5}$ 82°, ^{414c} b_{12} 94°; ^{361, 455} d 20/4 1.2386; n 20/D 1.5700.^{414c}

$\text{HOCH}_2\text{CH(SH)CH}_2\text{SH}$, $b_{0.4}$ 94°, ³⁶¹ $b_{0.5}$ 89°, ^{336, 343} $b_{0.8}$ 82–4°, ^{414c}

- b_1 87–9°, ^{105c} 81°, ⁷⁵ $b_{1.9}$ 80°, $b_{3.4}$ 90°, $b_{5.6}$ 100°, $b_{9.7}$ 100°, b_{15} 120°, b_{25} 130°, b_{40} 140°, ³³² b_8 100°; ¹²⁵ d_{17} 1.14, ^{105c} d 25/4 1.2385; ³³² n 15/D 1.5730, ¹²⁵ n 21/D 1.5710, ⁷⁵ n 25/D 1.5720; ³³² Ac., $b_{1.5}$ 90°; d 25/4 1.1916; n 25/D 1.5185; ³³⁰ propionyl, $b_{0.2}$ 70°; d 25/4 1.1491; n 25/D 1.5089; ³³⁰ butyryl, $b_{0.25}$ 78°; d 25/4 1.1095; n 25/D 1.5095; ³³⁰ diAc., $b_{0.05}$ 120°; ⁷⁵ triAc., $b_{0.1}$ 139°, ¹²⁵ $b_{0.5}$ 120°; ⁷⁵ n 20/D 1.5140; ¹²⁵ n 23/D 1.5105. ⁷⁵
 HOCH₂CH₂CH(SH)CH₂SH, b_1 96–7°, ³³⁰ $b_{0.0001}$ 70–1°; ^{299d} d 25/4 1.1842; ³³⁰ n 23/D 1.5572, ^{299d} n 25/D 1.5533; ³³⁰ OAc., $b_{0.0001}$ 65–6°; n 20/D 1.5208; triAc., $b_{0.0001}$ 110–12°; n 22/D 1.5150. ^{299d}
 HOCH₂CH(OH)CH(OH)CH₂SH, tetraAc., m .78°. ¹²⁵
 HSCH₂CH(OH)CH(OH)CH₂SH, *dl*-dithiothreitol, m .43°; b_2 125–30°; tetraAc., m .73°. ¹²⁵
 HSCH₂CH(OH)CH(OH)CH₂SH, dithioerythritol, m .83°; tetraAc., m .126°. ¹²⁵
 HOCH₂CH(OH)CH(OH)CH(SH)CH₂SH, pentaAc., m .92°. ¹²⁵
 (HOCH₂)₂C(CH₂SH)₂, m .98°, ¹³ 97°, ³³² 96°; ^{45a} tetraAc., $b_{0.0001}$ 110–20°; n 15/D 1.5092. ^{45a}
 HOCH₂CH(OH)CH(OH)CH(OH)CH(OH)CH₂SH, thiosorbitol., m .89–92°, ^{133a}, ^{254b} 93°. ¹³²
 HSCH₂CH(OH)CH(OH)CH(OH)CH(OH)CH₂SH, dithiomannitol, m .172°, ¹²⁵ 155–7°; $[\alpha]$ 20/D 1.86; ^{45a} hexaAc., m .188°. ¹²⁵
 2,5-Dithio-1,4:3,6-dianhydromannitol, m .16°; n 17/D 1.5692; $[\alpha]$ 18/D 85°. ^{45a}
 5,6-Dithiohexitol, hexaAc., m .87–9°. ^{45c}, ⁷⁵
 2-HOC₅H₈SH, *trans*, b_{35} 112–4°. ⁵⁶
 2-HOC₆H₁₀SH, *trans*, b_{15} 97–9°, ⁵⁶ b_{15} 92–4°; n 15/D 1.5190; ⁴⁶⁸ SAc., n 16/D 1.4897. ^{299d}
o-HOC₆H₄SH, b_{65} 134–6°, ^{323a} b .217°, ²⁵⁶ 216–7°. ¹⁸⁶
m-HOC₆H₄SH, m .17°; b_{35} 168°; diBz., m .78°. ⁴⁹⁹
p-HOC₆H₄SH, m .30°; ²⁵⁶, ⁴⁹⁹ b_1 105–10°, ²⁹⁰ b_{20} 144–6°; diAc., m .66°, ²⁵⁶ 67°; ⁴⁹⁹ Bz., m .75°; diBz., m .161°. ²⁹⁰
 3,4-Me(OH)C₆H₃SH, m .43°. ^{323a}
 3,5,4-Me₂(OH)C₆H₂SH, m .86°. ²³⁰
 2,3,5,4-Me₃(OH)C₆HSH, m .87°. ²³⁰
o-HOCH₂C₆H₄SH, benzoyl, m .126°. ³⁵⁵
 2,5-(HO)₂C₆H₃SH, m .118°. ⁴
 2,4-(HS)₂C₆H₃OH, oil, triBz., m .96°. ³⁴¹

2,4,6-(HS)₃C₆H₂OH, tetraBz., m.132°. ³⁴¹
 Dimercapto-*o*-cresol, m.51°; triBz., m.96°. ³⁴¹
 Dimercapto-*m*-cresol, m.69°; triAc., m.56°; triBz., m.120°. ³⁴¹
 Dimercapto-*p*-cresol, m.48°; triAc., m.98°; triBz., m.138°. ³⁴¹
 Trimercapto-*m*-cresol, m.36°; tetraAc., m.76°. ³⁴¹
 1-HOC₁₀H₈SH-4, m.114°; diAc., m.77°. ⁵⁰²
 1-HOC₁₀H₈SH-5, m.132°, ³⁵⁶ 115°. ⁴⁷⁷
 2-HOC₁₀H₈SH-6, m.137°; diAc., m.107°. ⁴⁹⁸
 2-HOC₁₀H₈SH-7, m.60–70°. ⁴⁷⁷

ETHER MERCAPTANS

MeOCH₂SH, m.–52.4°; b₁₅ 52°; d 0/4 1.1017, d 12/4 1.0733; n 12/D 1.4909; Ac., b₁₅ 94°; d 0/4 1.1977, d 27/4 1.1819; n 27/D 1.5178. ²⁵¹
 EtOCHMeSH, b₆₃ 38.6–8.8°, b₆₅ 38–9°; d 20/4 0.9160; n 20/D 1.4378; Ac., b.155–8°, b₁₇ 60–3.5°, ⁴⁰⁹ b₁₈ 62–2.5°, ³⁴⁵ b₂₁ 64.5°; ⁴⁰⁹ d 20/4 1.004; n 20/D 1.4556; Bz., b₄ 120–0.5°; d 20/4 1.0891; n 20/D 1.5472. ^{345, 409}
 BuOCHMeSH, b_{20.5} 52.5–3.5°, b₁₆ 48.2–8.3°; d 20/4 0.8984; n 20/D 1.4428; Ac., b.198–200°, b_{3-3.6} 61.7–2.3°, ⁴⁰⁹ b₇ 78–8.5°; ³⁴⁵ d 20/4 0.9664; n 20/D 1.4560; ^{345, 409} Bz., b_{3.2} 133.5–4.5°, ⁴⁰⁹ b₄ 139–40°; d 20/4 1.0492; ^{345, 409} n 20/D 1.5347, ⁴⁰⁹ 1.5346. ³⁴⁵
 MeOCH₂CH₂SH, b.112°, ⁷⁵ 109–10°; ¹⁷⁴ n 23/D 1.4488; Ac., b₁₁₀ 110°; n 18/D 1.4645. ⁷⁵
 (MeO)₂CHCH₂SH, b₁₃ 43–4°, ¹⁸² b₈₀ 81–2°; n 30/D 1.4463. ³²⁵
 EtOCH₂CH₂SH, b.125.5–5.8°, ⁴⁴⁵ 126–8°, ⁴⁰⁹ b₇₄₀ 125–6°, ³¹⁹ b₁₅ 37–40°, ³⁶⁹ b₄₁₅ 112–4°; ^{422b} d₂₀ 0.9412, ⁴⁰⁹ d 20/4 0.9462; ⁴⁴⁵ n 20/D 1.5795, ^{422b} 1.4456. ⁴⁰⁹
 (EtO)₂CHCH₂SH, b₁₃ 59°, ¹⁸² b₁₂ 59–60°, b₃₀ 81°, ²⁰² b₁₇ 68–72°; n 25/D 1.4392. ³²⁵
 PrOCH₂CH₂SH, b.134–4.5°, ⁴⁴⁵ b₁₇ 48–50°, ¹⁷⁴ b₄₀ 64–4.5°; d₂₀ 0.9227, ⁴⁰⁹ d 20/4 0.9222; ⁴⁴⁵ n 20/D 1.4478. ⁴⁰⁹
i-PrOCH₂CH₂SH, b₄₄ 56.1–6.4°; d₂₀ 0.9136; n 20/D 1.4424. ⁴⁰⁹
 BuOCH₂CH₂SH, b.156–7°, ⁴⁴⁵ 165–7°, b₁₈ 68–9°; d 20/4 0.9111, ³⁴⁴ 0.9161; ⁴⁴⁵ n 20/D 1.4488. ³⁴⁴
i-BuOCH₂CH₂SH, b₉ 45.2–5.5°; d₂₀ 0.9038; n 20/D 1.4444. ⁴⁰⁹
i-AmOCH₂CH₂SH, b₆ 53.9–4.5°; d₂₀ 0.9028; n 20/D 1.4489. ⁴⁰⁹
 HexOCH₂CH₂SH, b_{4.5} 103°; d₂₀ 0.8906; n 20/D 1.4556. ⁴⁰⁹
c-HexOCH₂CH₂SH, b_{4.5} 73–3.5°; d₂₀ 0.9938; n 20/D 1.4864. ⁴⁰⁹
 PhOCH₂CH₂SH, b₂₉ 134°; n 23/D 1.5597. ⁷⁵

- $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$, b_1 78–80°. ⁶⁶
 $\text{EtOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$, b_{20} 90°; n 20/D 1.4540. ^{422b}
 $\text{EtOCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_{20} 52–4°. ³⁶⁹
 $\text{BuOCMe}_2\text{CH}_2\text{SH}$, $b_{4.5}$ 59–61°; n 20/D 1.4493. ^{422b}
 $\text{AmOCMe}_2\text{CH}_2\text{SH}$, b_2 58–9°; n 20/D 1.4543. ^{422b}
 $\text{HexOCMe}_2\text{CH}_2\text{SH}$, b_2 73–4°; n 20/D 1.4536. ^{422b}
 $\text{HepOCMe}_2\text{CH}_2\text{SH}$, b_3 86°; n 20/D 1.4551. ^{422b}
 $\text{OctOCMe}_2\text{CH}_2\text{SH}$, $b_{3.5}$ 98–102°; n 20/D 1.4548. ^{422b}
 $\text{MeOCH}_2\text{CH}_2\text{CH}:\text{CHCH}_2\text{SH}$, b_7 63–6°; d 20/4 0.9783; n 20/D 1.4775. ³⁴⁷
 $\text{EtOCH}_2\text{CH}_2\text{CH}:\text{CHCH}_2\text{SH}$, b_8 70–1°; d 20/4 0.9530; n 20/D 1.4725. ³⁴⁷
 $\text{BuOCH}_2\text{CH}_2\text{CH}:\text{CHCH}_2\text{SH}$, b_{11} 107–10°; d 20/4 0.9232; n 20/D 1.4675. ³⁴⁷
 $\text{MeOCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, b_1 68°, ³³⁶ b_6 63–5°; ³³¹, ^{422a} d 25/4 1.1102; n 25.5/D 1.5178. ³³¹
 $\text{EtOCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, b_6 75–7°; d 25/4 1.0692; n 25/D 1.5049. ³³¹
 $i\text{-PrOCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{5.5}$ 75–6°; d 25/4 1.0249; n 25/D 1.4930. ³³¹
 $\text{BuOCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.5}$ 62°; d 25/4 1.0181; n 25/D 1.4958. ³³¹
 $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.02}$ 155°; n 15/D 1.5390; tetraAc., $b_{0.001}$ 169–74°; n 17/D 1.5035. ¹²⁶
 $\text{MeOCH}_2\text{CH}(\text{OMe})\text{CH}_2\text{OCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.0001}$ 95°; n 25/D 1.4995; diAc., $b_{0.001}$ 120°; n 20/D 1.5040. ^{299a}
 $(\text{HOCH}_2)_2\text{CHOCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.005}$ 150–1°; n 22/D 1.5445; tetraAc., $b_{0.003}$ 175–6°; n 18/D 1.5017. ¹²⁶
 $\text{MeOCH}_2\text{CH}(\text{OH})\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{1.5}$ 82°; n 15/D 1.5100; diAc., $b_{0.5}$ 110°; n 20/D 1.5098. ^{299a}
 $\text{MeOCH}_2\text{CH}(\text{OMe})\text{CH}(\text{OMe})\text{CH}(\text{SH})\text{CH}_2\text{SH}$, $b_{0.0001}$ 75°; n 20/D 1.5020; diAc., $b_{0.0001}$ 90–7°; n 22/D 1.5045. ^{299a}
 $\text{O}(\text{CH}_2\text{CH}_2\text{SH})_2$, m . –80°; ²⁹⁸ $b_{.217^\circ}$, ¹¹, ¹² $b_{0.05}$ 53–4°, ⁴¹³ b_{10} 90–1°, ³⁶⁰ $b_{12.7}$ 95–5.3°, ²¹¹ b_{18} 103–4°; d 0/4 1.1854, d 25/4 1.1648, ²⁹⁸ d 20/4 1.125; ⁴¹³ n 20/D 1.5339; ²⁹⁸ $p\text{-NO}_2\text{Bz.}$, m . 106.5°. ³⁶⁰
 $\text{O}(\text{CHMeCH}_2\text{SH})_2$, $b_{0.55}$ 52–4°; d 20/4 1.051. ⁴¹³
 $\text{O}(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_2$, $b_{12.7}$ 99–101°, ²¹¹ $b_{0.12}$ 63–4°; d 20/4 1.053. ⁴¹³

$\text{O}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH})_2$, b_6 164–7°; d 25/4 1.1169; n 25/D 1.4981.³⁵³

3,4-MeO(HO)C₆H₃CH₂CH₂CH₂SAc, $b_{1.5}$ 180°.⁶⁵

o-MeOC₆H₄SH, b_{219}° .¹⁵⁷

m-MeOC₆H₄SH, b_4 78°; n 20/D 1.5845.⁴⁵¹

p-MeOC₆H₄SH, b_{227}° ,¹⁵⁷ 227–9°,⁴⁴⁷ b_5 89–90°; d 25/4 1.1313; n 25/D 1.5801; ⁴⁴¹ Ac., m_{100}° .⁴⁴⁷

o-EtOC₆H₄SH, b_{227}° .¹⁵⁷

p-EtOC₆H₄SH, m_{41}° ; ²⁵⁶ b_{238}° ,¹⁵⁷ 223–6°,⁴⁴⁷ 275–7°; ²⁵⁶ Ac., m_{41}° ; Bz., 106° .⁴⁴⁷

2,5-MeOMeC₆H₃SH, b_{245}° .¹⁵⁷

p-MeOC₆H₄CH₂SH, $b_{2.5}$ 89–94°; n 25/D 1.5660; (O₂N)₂ Bz., m_{102}° .²⁶⁵

$\text{O}(\text{C}_6\text{H}_4\text{SH}-p)_2$, m_{98}° ; diAc., m_{68}° .⁴⁶⁵

MeOC₆H₃(SH)₂-2,4, m_{51}° .¹⁵⁸

p-MeOC₆H₄SeH, Bz., m_{97}° .⁴⁴⁷

p-EtOC₆H₄SeH, b_{24} 156–8°; Bz., m_{95}° .⁴⁴⁷

HALO-MERCAPTANS

ClCH₂SH, Ac., b_{22} 62–3°.⁵⁰

Cl₃CSH, b_{15} 125°.⁹⁴

F₃CSH, $b_{-36.7}^\circ$.¹⁹⁸

ClCH₂CH₂SH, b_{13} 43°, b_{25} 60°,¹⁰⁷ b_{125-6}° ,^{34b} 93–108°; ⁴⁶⁹ d 0/4 1.218,¹⁰⁷ 1.225, d 20/4 1.203,^{34b} d 21/4 1.193; ¹⁰⁷ n 15/D 1.514,¹⁰⁷ n 20/D 1.5289; ^{34b} Ac., b_4 51°; d_{20} 1.204.⁶³

BrCH₂CH₂SH, b_{28} 50–1°.¹⁰⁷

ICH₂CH₂SH, Ac., b_{10} 97°; d 17/4 1.8195; n 17/D 1.5190.²²⁴

FCH₂CH₂SH, b_{225} 38.5°; d 25/4 1.082; n 25/D 1.4282; Ac., b_{100} 87°; d 25/4 1.4041; n 25/D 1.4525.¹²²

ClCHMeCH₂SH, b_{125}° ,^{414c} 124–5°,^{102a} b_{82} 60–2°; ⁴³² d_{20} 1.1062; ^{414c} n 12/D 1.484,^{102a} n 20/D 1.4844,⁴³² 1.4852; ^{414c} Ac., b_9 70–1°.^{102a}

BrCHMeCH₂SH, Ac., $b_{0.2}$ 45°; n 23/D 1.52.^{102a}

ClCH₂CH₂CH₂SH, b_{12} 52°, b_{760} 145.5°; d_{20} 1.1280; n 20/D 1.4930; Ac., b_{10} 83–4°; d 20/4 1.1589; n 20/D 1.4954.^{414b}

BrCH₂CH₂CH₂SH, b_{12} 55–6°; Bz., b_1 148–9°; d 25/4 1.4129; n 25/D 1.5950.²²⁹

ClCH₂CH(OH)CH₂SH, $b_{1.3}$ 57°,^{414b} 60°; ^{414a} d_{20} 1.2981; ^{414a}, ^{414b}

n 20/D 1.5265,^{414b} 1.5257; ^{414a} Ac., $b_{0.4}$ 94°; b_1 100–1°; d_{20} 1.2806; n 20/D 1.5186; β -Ac., b_1 69–70°; d_{20} 1.2308; n 20/D 1.4855; diAc., $b_{0.9}$ 95°, b_1 102–3°; d_{20} 1.2328, 1.2330; n 20/D 1.4886, 1.4890.^{414b}
 ClCH₂CHClCH₂SH, b_{20} 74–6°; n 15/D 1.5245; Ac., b_{25} 122°; n 20/D 1.5155.^{102b}
 ClCH₂CH₂CH(SH)CH₂SH, $b_{0.0001}$ 92°; n 15/D 1.5392.^{299d}
 ClCH₂CH₂SCH₂CH₂SH, b_{20} 120–7°.¹⁰⁷
 2-ClC₅H₈SH, chlorocyclopentanethiol; *trans*, b_{12} 60–1.5°.⁴⁶⁸
 Cl₅C₆SH, m.248°.⁴⁴⁸

SULFIDE-MERCAPTANS

EtSCH₂SH, b_{18} 64–6°.⁵¹
 MeSCH₂CH₂SH, b_{15} 57–61°,¹⁷⁴ b_{40} 82°.²⁹⁷
 EtSCH₂CH₂SH, $b_{0.6}$ 37°,³⁵⁸ b_{50} 93°,²⁵⁵ b_{188} °.¹⁰⁸
 PrSCH₂CH₂SH, b_{11} 75–7°.¹⁷⁴
 BuSCH₂CH₂SH, b_{10} 90–2°.¹⁷⁴
 AmSCH₂CH₂SH, b_5 105°.²⁹⁷
 EtSCH₂CHMeSH, $b_{0.8}$ 68–70°.³⁵⁸
 EtSCH₂CH₂SCH₂CH₂SH, $b_{0.6}$ 103–5°.³⁵⁸
 EtSCH₂CHMeSCHMeCH₂SH, $b_{0.6}$ 102–10°.³⁵⁸
 2-BuSC₆H₁₀SH, $b_{2.5}$ 109–11°; n 20/D 1.5234.^{422b}
 2-AmSC₆H₁₀SH, $b_{3.5}$ 123–6°; n 20/D 1.5186.^{422b}
 2-HexSC₆H₁₀SH, b_3 130–3°; n 20/D 1.5135.^{422b}
 2-HepSC₆H₁₀SH, b_3 141–4°; n 20/D 1.5113.^{422b}

 S(CH₂CH₂SH)₂, m.–11°,²⁹⁶ –12.5°;²⁹⁸ b_5 102–2.5°,³⁵² b_{10} 135–6°,²⁹⁸ b_{13} 138°,²⁹⁶ b_{18} 135–7°;¹⁹¹ d 20/4 1.1908,²⁹⁶ d 25/4 1.1797;³⁵² *p*-nitrobenzoate m.119.4°.³⁶⁰
 (•CH₂SCH₂CH₂SH)₂, m.46°,¹⁹¹ 15–7°; b_{10} 168–72°.²⁹⁸
 S(CH₂CH₂CH₂SH)₂, m.–8°; b_6 138–40°; d 0/4 1.1612, d 25/4 1.1456; n 20/D 1.5740.²⁹⁸
 S(CH₂CH₂OCH₂CH₂SH)₂, b_8 182–5°.²⁹⁸
 CH₂(CH₂SCH₂CH₂SH)₂, $b_{3.5}$ 189–90°.³⁵²
 O₂S(CH₂CH₂SCH₂CH₂SH)₂, m.81°.³⁵²
p,p'-HSC₆H₄SC₆H₄SH, m.114°; diAc., m.65°.⁴⁶⁶
 HOCH₂CH₂SCH₂CH₂SH, $b_{0.5}$ 106°; n 19/D 1.5622; OAc., $b_{0.5}$ 98–100°; n 15/D 1.5629; SAc., $b_{0.4}$ 108–10°; n 20/D 1.5338.^{299d}
 HOCH₂CH(SH)CH₂SCH₂CH(SH)CH₂SH, $b_{0.001}$ 150–6°; n 15/D 1.6190.^{299d}
 2-HOC₆H₁₀SC₆H₁₀SH-2, $b_{0.2}$ 150–60°.^{299d}

ALDEHYDE AND KETO-MERCAPTANS

- $\text{HSCH}_2\text{CH}_2\text{CHO}$, Ac., b_{11} 89° ; n 25/D 1.4887; ⁴⁷² b_1 $66-70^\circ$; n 20/D 1.5079.⁶⁵
 $\text{HSCH}_2\text{CHMeCHO}$, Ac., b_2 65° ; n 25/D 1.4831.⁴⁷²
 $\text{HSCMeCH}_2\text{CHO}$, Ac., b_2 $59-60^\circ$; n 20/D 1.5025.⁶⁵
 $\text{HSCPhCH}_2\text{CHO}$, $m.44^\circ$; b_1 $115-7^\circ$.⁶⁵
 HSCH_2COMe , two forms $m.82^\circ$ and $109-11^\circ$,⁴⁰³ $109-11^\circ$,²⁰⁸ $105-11^\circ$,³¹⁶ 109° ; ²²⁵ Ac., b_2 $130-40^\circ$; ³¹⁶ Bz., $m.8^\circ$; $b_{0.05}$ $90-100^\circ$.²⁰⁸
 $\text{Me}_2\text{CHCH}(\text{SH})\text{COMe}$, b_{56} 60° .¹³⁹
 $\text{HSCMe}_2\text{CH}_2\text{COMe}$, b_8 $84-6^\circ$,⁶⁵ b_{12} 55° ; semicarbazone, $m.160^\circ$.⁹
 $\text{HSCPhCH}_2\text{COMe}$, $m.68^\circ$.⁶⁵
 $\text{HSC}(\text{CHMe}_2)\text{CH}_2\text{CH}_2\text{COMe}$, $m.69^\circ$; Ac., b_{10} 134° .²⁸
 $\text{HSCH}_2\text{COC}_6\text{H}_{13}$, $m.44^\circ$.²²⁵
 $p\text{-PhC}_6\text{H}_4\text{COCH}_2\text{SH}$, $m.109^\circ$.¹⁷⁷
 PhCOCHPhSH , $m.42-4^\circ$; Bz., $m.112^\circ$.⁴⁰²
 $m\text{-MeCOC}_6\text{H}_4\text{SH}$, b_{11} 137° ; Bz., b_{11} $135-6^\circ$.⁴⁰⁶
 $p\text{-MeCOC}_6\text{H}_4\text{SH}$, $m.28.5^\circ$; ²⁰⁰ b_{11} 142° ,⁴⁰⁶ $b_{2.5}$ 110° ; n 25/D 1.6181; ⁴⁵¹ Bz., $m.50^\circ$.⁴⁰⁶
 $4,3\text{-MeCO}(\text{MeO})\text{C}_6\text{H}_3\text{SH}$, $m.80^\circ$.²⁰⁰
 $\text{HSCH}_2\text{COCH}_2\text{SH}$, $m.86^\circ$; b_{14} 95° .⁴⁰³
 $\text{MeCOC}_6\text{H}_3(\text{SH})_{2-2,4}$, $m.215^\circ$.³⁶⁴
 $\text{MeCOC}_6\text{H}_3(\text{SH})_{2-3,5}$, $m.128^\circ$.³⁶⁴
 $\text{PhCOCH:C}(\text{SH})_2$, $m.64^\circ$.²³¹
 $p\text{-MeOC}_6\text{H}_4\text{COCH:C}(\text{SH})_2$, $m.85^\circ$; Bz., $m.125^\circ$.²³²
 $(p\text{-HSC}_6\text{H}_4)_2\text{CO}$, $m.165^\circ$.⁴⁴⁸

AMINO-MERCAPTANS

- $\text{CH}_2(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{SH}$, $m.12.5-15^\circ$; HCl, $m.195-205^\circ$.⁴²
 $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{SH}$, $m.86-8^\circ$.⁴²
 $\text{H}_2\text{NCH}_2\text{CH}_2\text{SH}$, $m.100^\circ$,¹⁵⁰ 98.5° ,⁵⁴ 98° ,⁴¹ 85° ; ¹⁹⁷ $b.130^\circ$; ⁴¹ HCl, $m.70.7^\circ$,⁵⁴ 72° ; ^{149a}, ¹⁵² picrate, $m.126^\circ$; ¹⁵⁰ formyl, b_{747} 138° ; ^{149b} NAc b_7 $138-40^\circ$; ¹⁹ SA., HCl, $m.137^\circ$; ⁴⁸⁷ diAc., $m.30^\circ$,¹⁹⁷ 28° ; $b_{0.00001}$ 100° ,¹⁸ b_1 $131-3^\circ$,¹⁹⁷ b_{15} $181-3^\circ$; ¹⁹ n 27/D 1.5070.¹⁹⁷
 $\text{H}_2\text{NCH}_2\text{CHMeSH}$, $m.65^\circ$; ^{149b} $b.158^\circ$; ³⁰⁶ HCl, $m.88$; picrate, $m.144^\circ$.¹⁵²
 $\text{H}_2\text{NCHMeCH}_2\text{SH}$, HCl, $m.94^\circ$; picrate, $m.193^\circ$.⁵²
 $\text{H}_2\text{NCH}_2\text{CMe}_2\text{SH}$, HCl, $m.203^\circ$.⁹⁶
 $\text{HepNHCH}_2\text{CH}_2\text{SH}$, $b_{2.5}$ $70-1^\circ$; n 20/D 1.4703; Ac., b_4 $160-2^\circ$.^{422a}
 $\text{DodecNHCH}_2\text{CH}_2\text{SH}$, $b_{2.5}$ $141-3^\circ$.²¹⁶

- PhNHCH₂CH₂SH, b_3 119°, ^{216, 359} $b_{2.5}$ 95–7°; n 20/D 1.6040; Ac., $m. 66^\circ$.^{299a}
- o*-MeC₆H₄NHCH₂CH₂SH, b_3 116°. ²¹⁶
- β -C₁₀H₇NHCH₂CH₂SH, b_3 184°. ²¹⁶
- BuNHCHMeCH₂SH, b_1 40–2°. ²¹⁶
- c*-HexNHCHMeCH₂SH, b_1 66–8°. ²¹⁶
- PhNHCHMeCH₂SH, b_1 95°. ²¹⁶
- PhCH₂NHCHMeCH₂SH, b_1 92–4°. ²¹⁶
- HeptNHCH₂CMe₂SH, b_2 83–6°; n 15/D 1.4630; ^{421b, 422a} Ac., $b_{2.5}$ 128–31; n 15/D 1.4800. ^{422a}
- DodecNHCH₂CMe₂SH, b_3 138–41°. ^{422a}
- MeNHCHMeCHPhSH, $m. 48^\circ$. ⁶²
- PhNHCH₂CH₂CH₂SH, b_1 95°. ³⁵⁹
- Me₂NCH₂CH₂SH, Ac., $m. 95^\circ$; ³⁵⁷ MeI, $m. 205^\circ$, ²²⁴ 204°, ³⁵⁷ 203°; ⁴⁴⁴ MeCl, $m. 238^\circ$. ¹⁹⁰
- Et₂NCH₂CH₂SH, b_4 46–8°, ⁹¹ b_{20} 64–6°, ¹⁷² 64–5°, ¹⁸¹ b_{21} 65°, b_{32} 74°; d 20/4 0.8751; ¹⁷¹ n 20/D 1.4670, ² 1.4680; ¹⁷¹ HCl, $m. 173^\circ$, ² 170–2°. ¹⁷¹
- Bu₂NCH₂CH₂SH, b_2 73–4°, ^{216, 359} 74–5°, ^{422a} b_{26} 138°; ⁹¹ n 20/D 1.4635; HCl, $m. 123^\circ$. ^{422a}
- Am₂NCH₂CH₂SH, $b_{2.5}$ 86–90°; n 20/D 1.4643; HCl, $m. 86^\circ$. ^{422a}
- Hept₂NCH₂CH₂SH, b_2 127–8°; n 20/D 1.4660. ^{422a}
- Oct₂NCH₂CH₂SH, b_2 146–8°; n 20/D 1.4658. ^{422a}
- (CH₂)₅NCH₂CH₂SH, $b_{1.5}$ 50–1°, ^{216, 359} b_4 56–7°, b_9 70–2°, ^{299a} b_{11} 85°; n 20/D 1.5015, ^{422a} n 25/D 1.4995. ⁹¹
- O(CH₂CH₂)₂NCH₂CH₂SH, b_{12} 106°, b_{15} 100°; n 25/D 1.5030. ⁹¹
- 2-Methylpyrrolidyl CH₂CH₂SH, b_{11} 74–4.5°; n 25/D 1.4898. ^{88, 90}
- 2-Methylpiperidyl CH₂CH₂SH, b_{14} 96.5–70°; n 25/D 1.4974. ^{88, 90}
- MeDodecNCH₂CH₂SH, $b_{2.5}$ 139–40°. ^{216, 359}
- MePhNCH₂CH₂SH, $b_{2.5}$ 116°. ^{216, 359}
- Me₂NCH₂CHMeSH, $b. 153$ –4°; MeCl, $m. 92^\circ$; MeI, $m. 145^\circ$. ³⁵⁷
- Am₂NCH₂CHMeSH, b_2 86–7°; n 20/D 1.4634. ^{422a}
- Et₂NCH₂CMe₂SH, b_{52} 94–5°; n 15/D 1.4597. ^{422a}
- Bu₂NCH₂CMe₂SH, b_2 89–90°; n 15/D 1.4748. ^{422a}
- Am₂NCH₂CMe₂SH, b_2 85–90°; n 15/D 1.4653; HCl, $m. 86^\circ$. ^{422a}
- i*-Am₂NCH₂CMe₂SH, b_2 83–6°; n 20/D 1.4677. ^{422a}
- Hept₂NCH₂CMe₂SH, $b_{2.5}$ 124–6°. ^{421b, 422a}
- (CH₂)₅NCH₂CMe₂SH, $b_{1.5}$ 53–6°, ^{421b} $b_{2.5}$ 47°; n 20/D 1.4840, ^{422a} 1.4848; ^{421b} HCl, $m. 199^\circ$. ^{422a}

3-Methylpiperidyl $\text{CH}_2\text{CMe}_2\text{SH}$, b_2 51–3°, ^{422a} $b_{2.5}$ 49–57°; ^{421b} n 20/D 1.4782. ^{421b}, ^{422a}

4-Ethylpiperidyl $\text{CH}_2\text{CMe}_2\text{SH}$, $b_{2.5}$ 74–6°; n 20/D 1.4894. ^{421b}, ^{422a}

$\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{CMe}_2\text{SH}$, $b_{6.5}$ 81–2°; n 20/D 1.4886. ^{422a}

$\text{Me}_2\text{NCH}_2\text{CHPhSH}$, b_1 80°. ⁶²

$\text{PhNHCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_1 95°. ³⁵⁹

$\text{Et}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_{15} 80°, ²⁵⁰ b_{28} 76–7.5°; d 20/4 0.8908; n 20/D 1.4668, ¹⁷¹ n 25/D 1.4650; ²⁵⁰ HCl , m . 76°. ¹⁷¹

$\text{Bu}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_2 112°; n 25/D 1.4994. ⁹¹

$\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_{11} 110–2°; n 25/D 1.4962; ⁸⁸, ⁹⁰ picrate, m . 130°. ⁹⁰

2-Methylpiperidyl $\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$, b_6 95.5°; n 25/D 1.4950; picrate, m . 116–8°. ⁹⁰

$\text{Me}_2\text{N}(\text{CH}_2)_4\text{SH}$, b_{35} 84°. ³⁰⁵

$\text{Et}_2\text{N}(\text{CH}_2)_4\text{SH}$, b_{15} 95–6°; n 20/D 1.4678. ²⁵⁰

$\text{Et}_2\text{N}(\text{CH}_2)_3\text{CHMeSH}$, b_{11} 94°; n 25/D 1.4630; picrate, m . 62–5°. ⁸⁹

$(\text{CH}_2)_5\text{N}(\text{CH}_2)_4\text{SH}$, b_{10} 93°; n 20/D 1.5000. ²⁵⁰

$\text{H}_2\text{NCH}_2\text{CH}(\text{SH})\text{CH}_2\text{SH}$, b_1 65–75°, ³³⁶, ³⁴³ 80°. ^{433a}

$\text{MeN}(\text{CH}_2\text{CH}_2\text{SH})_2$, b_{11} 105–7°. ¹⁹¹

$\text{EtN}(\text{CH}_2\text{CH}_2\text{SH})_2$, b_4 108–9°. ¹⁹¹

$\text{PhN}(\text{CH}_2\text{CH}_2\text{SH})_2$, b_2 138–40°, ^{422a} $b_{2.5}$ 171°; ²¹⁶ n 20/D 1.6248. ^{422a}

$\text{BuN}(\text{CHMeCH}_2\text{SH})_2$, $b_{0.5}$ 85–6°. ²¹⁶

$c\text{-HexN}(\text{CHMeCH}_2\text{SH})_2$, b_1 127°. ²¹⁶

$\text{HSCMe}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\text{CMe}_2\text{SH}$, m . 127–31°. ^{421b}

$\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$, b_7 147°. ¹⁹¹

$\text{Bu}_2\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$, b_2 129–30°. ²¹⁶, ³⁵⁹

$\text{PhNHCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH}$, $b_{2.5}$ 171°. ²¹⁶

AROMATIC AMINO-MERCAPTANS

$o\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$, b_6 125–7°. ²³⁷

$m\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$, b_{16} 180–90°; diAc. , m . 97°. ⁵⁰¹

$p\text{-NH}_2\text{C}_6\text{H}_4\text{SH}$, m . 46°, ⁵⁰⁰ 43–5°; ¹⁷⁰ b_{15} 140–5°, ⁵⁰⁰ b_{17} 143–6°; ¹⁷⁰ NAc. , m . 163°. ²⁵⁶

$o\text{-MeNHC}_6\text{H}_4\text{SH}$, b_{18} 126–7°, b_{30} 142–3°. ²³⁵

$o\text{-PhNHC}_6\text{H}_4\text{SH}$, b_8 174–5°. ²³⁶

$o\text{-PhCH}_2\text{NHC}_6\text{H}_4\text{SH}$, m . 37°; b_{30} 179°. ²³⁵

- o -HO₂CCH₂NHC₆H₄SH, m.132°. ²³⁵
 p -Me₂NC₆H₄SH, m.28.5°; b.259–60°, ²⁵⁶ b₂ 122°. ¹⁶⁹
 2,4-(H₂N)₂C₆H₃SH, triAc., m.245° decomposes. ^{205b}
 2,4-H₂N(O₂N)C₆H₃SH, m.183°; ¹⁴⁵ diAc., m.150°. ^{205a}
 2,5-H₂N(O₂N)C₆H₃SH, m.81°. ⁹³
 2,4-H₂N(Br)C₆H₃SH, HCl, m.219°. ²²
 2,4-H₂N(Cl)C₆H₃SH, m.201°. ²⁴⁸
 2,4,5-H₂NCl(HO)C₆H₂SH, HCl, m.225°. ¹⁴⁵
 4-H₂NC₁₀H₆SH, m.93°; Ac., m.173°; diAc., m.152°. ⁵⁰³
 2-Mercaptopyridine, m.124°. ⁴⁵⁸
 3-Mercaptopyridine, m.77°. ⁴²⁹
 3-Mercaptomethylpyridine, b₁₃₋₅ 121°, b₁₇₋₈ 118–25°. ⁴⁷¹
 2-(β-Mercaptoethyl)pyridine, b_{7.0} 94°; Ac., b_{1.0} 95–7°; n 25/D 1.5480. ⁴⁷²
 2-(β-Mercaptoethyl)-5-ethylpyridine, Ac., b_{9.5} 131–6°; d 25/4 1.0664; n 25/D 1.5377. ⁴⁷²
 2-Mercapto-3,5-diiodopyridine, m.206.5°. ²⁴⁰
 4-Mercapto-3,5-diiodopyridine, m.205°. ²⁴⁰
 2-Mercaptoquinoline, m.174°. ³⁷⁰
 2-Mercapto-3-methylquinoline, m.253°. ³⁷⁰
 4-Mercaptoquinoline, m.187°. ³⁷⁰

MISCELLANEOUS MERCAPTANS

- HSCH₂CH₂CN, b₁₅ 75°; d₂₀ 1.0696; n 20/D 1.4877; Ac., b₃ 94°; d₂₀ 1.1212; n 20/D 1.4912. ⁹⁷
 p -HSC₆H₄SO₃H, m.252°. ³²¹

BIBLIOGRAPHY

1. Kiuji Abe, J. Chem. Soc. Japan, 65, 204–9, 414–8, 650–4 (1944)—C.A. 41, 4197.
2. N. F. Albertson and R. O. Clinton, J. Am. Chem. Soc., 67, 1222–3 (1945)—C.A. 39, 4064.
3. Otto Albrecht and Richard Sallmann to Soc. ind. chim. à Bâle, U.S. pat. 2,337,220 (1943)—C.A. 38, 3488.
4. W. Alcalay, Helv. chim. acta, 30, 578–84 (1947)—C.A. 41, 4122.
5. W. N. Aldridge, Biochem. J., 42, 52–8 (1948)—C.A. 42, 8865.
6. A. L. Alvarado and E. I. du Pont de Nemours & Co., Brit. pat. 578,124 (1946)—C.A. 41, 2429.

7. M. L. Amdur, *Occupational Med.*, **3**, 386-91 (1947)—C.A. **41**, 7016.
8. V. P. Argiles, *Trabajos inst. nacl. cienc. med. (Madrid)*, **11**, 177-203 (1948)—C.A. **43**, 331.
9. Fritz Arndt, R. Schwarz, C. Martius, and E. Aron, *Rev. faculte sci. univ. Istanbul*, **A13**, 57-77 (1948)—C.A. **42**, 4176.
10. L. von Babo and M. Hirschbrunn, *Ann.*, **84**, 10 (1852).
11. H. J. Backer and J. Kramer, *Rec. trav. chim.*, **53**, 1101-12 (1934)—C.A. **29**, 1061.
12. H. J. Backer and F. Stienstra, *Rec. trav. chim.*, **52**, 1033-8 (1933)—C.A. **28**, 4714.
13. H. J. Backer and A. F. Tamsa, *Rec. trav. chim.*, **57**, 1183-1210 (1938)—C.A. **33**, 1679.
14. H. J. Backer and G. L. Wiggerink, *Rec. trav. chim.*, **60**, 453-73 (1941)—C.A. **36**, 5824.
15. Z. M. Bacq, *Bruxelles med.*, **27**, 2111-8 (1947); *Chimie & industrie*, **59**, 468 (1948)—C.A. **43**, 3974.
16. Z. M. Bacq, P. Fischer, and J. Lecomte, *Arch. intern. Physiol.*, **56**, 25-7 (1948)—C.A. **43**, 3143.
17. Z. M. Bacq, J. Lecomte, and P. Fischer, *Compt. rend. soc. biol.*, **142**, 1068 (1948)—C.A. **43**, 3563.
18. J. Baddiley and E. M. Thain, *J. Chem. Soc.*, **1951**, 2253-8, 3425-6—C.A. **46**, 8008.
19. Badische Anilin- & Soda-Fabrik (Richard Kuhn and Günter Quadbeck), *Ger. pat.* 893,795 (1953)—C.A. **48**, 12792.
20. R. H. Baker and Charles Barkenbus, *J. Am. Chem. Soc.*, **58**, 262-4 (1936)—C.A. **30**, 2961.
21. S. A. Ballard, D. S. Melstrom, and C. W. Smith, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 973-1003.
22. Richard Baltzly, Morton Harfenist, and F. J. Webb, *J. Am. Chem. Soc.*, **68**, 2673-8 (1946)—C.A. **41**, 2059.
23. Jean W. Barnett, *J. Chem. Soc.*, **1944**, 5-8—C.A. **38**, 2010.
24. E. S. G. Barron and G. Kalinsky, *Biochem. J.*, **41**, 346-51 (1947)—C.A. **42**, 3003.
25. E. S. G. Barron, Zelma B. Miller, G. R. Barlett, J. Meyer, and T. P. Singer, *Biochem. J.*, **41**, 69-74 (1947)—C.A. **41**, 4522.
26. E. S. G. Barron, Zelma B. Miller, and G. Kalnitsky, *Biochem. J.*, **41**, 62-8 (1947)—C.A. **41**, 4774.
27. E. S. G. Barron, Zelma B. Miller, and J. Meyer, *Biochem. J.*, **41**, 78-82 (1947)—C.A. **41**, 4523.

28. L. Bateman and R. W. Glazebrook, *Chemistry & Industry*, 1951, 1093—C.A. 47, 3847.
29. Randolph Batson and J. C. Peterson, *Ann. Internal Med.*, 29, 278-93 (1948)—C.A. 42, 8343.
30. E. Baumann, *Ber.*, 23, 1869-76 (1890).
31. O. K. Behrens, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 657-79.
32. J. B. Belogorsky and Donald Slaughter, *Proc. Soc. Exptl. Biol. Med.*, 72, 196-8 (1949)—C.A. 44, 2117.
33. P. Benigno, *Arch. intern. pharmacodynamie*, 77, 5-16 (1948)—C.A. 43, 1456.
34. G. M. Bennett, (a) *J. Chem. Soc.*, 119, 418-25 (1921); (b) *ibid.*, 121, 2139-46 (1922)—C.A. 15, 2061; 17, 61.
35. G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, 1927, 1666-76, 1676-84—C.A. 21, 3191.
36. G. M. Bennett and A. L. Hock, *J. Chem. Soc.*, 127, 2671-7 (1925); 1927, 2496-9—C.A. 20, 362; 22, 381.
37. G. M. Bennett and Edith M. Whincop, *J. Chem. Soc.*, 119, 1860-4 (1921)—C.A. 16, 409.
38. R. W. Berliner, J. J. Kennedy, Jr., and J. G. Hilton, *Am. J. Physiol.*, 154, 537-41 (1948)—C.A. 43, 1870.
39. Didier Bertrand, *Compt. rend.*, 227, 91-3 (1948); *Bull. soc. chim. biol.*, 31, 185-90 (1949)—C.A. 42, 8236; 43, 6253.
40. Herbert Bestian to I. G. Farben., *Ger. pat.* 710,276 (1941)—C.A. 37, 3768.
41. Herbert Bestian, J. Heyna, A. Bauer, G. Ehlers, B. Hirsekorn, T. Jacobs, W. Noll, W. Weibezahn, and F. Römer, *Ann.*, 566, 210-44 (1950)—C.A. 44, 5806.
42. Arthur Binz and L. H. Pence, *J. Am. Chem. Soc.*, 61, 3134-9 (1939)—C.A. 34, 435.
43. Arthur Binz, C. Räth, and E. Walter, *Ber.*, 57, 1398-1403 (1924)—C.A. 19, 237.
44. C. B. Biswell to Du Pont Co., *U.S. pat.* 2,436,137 (1948)—C.A. 42, 3430.
45. Peter Bladon and L. N. Owen, (a) *J. Chem. Soc.*, 1950, 585-90; (b) *ibid.*, 591-97; (c) *ibid.*, 598-603—C.A. 44, 6811, 6812, 6813.
46. W. D. Block, O. H. Buchanan, and R. H. Freyberg, *J. Pharmacol.*, 76, 355-7 (1942)—C.A. 37, 1194.
47. W. D. Block, Naomi C. Geib, and W. D. Robinson, *J. Lab. Clin. Med.*, 33, 1381-92 (1948)—C.A. 43, 2328.

48. D. C. Blood and I. G. White, *Australian J. Sci.*, **9**, 151 (1947)—C.A. **41**, 6992.
49. Horst Böhme, *Ber.*, **69**, 1610-5 (1936)—C.A. **30**, 6323.
50. Horst Böhme, *Ger. pat.* 869,064 (1953)—C.A. **48**, 11485.
51. Horst Böhme, Harriet Fischer, and Rudolf Frank, *Ann.*, **563**, 54-72 (1949)—C.A. **43**, 7409.
52. Margarethe Boese, *Ber.*, **53**, 2000-2 (1920)—C.A. **15**, 1138.
53. M. T. Bogert and R. W. Allen, *Ind. Eng. Chem.*, **18**, 532-3 (1926)—C.A. **20**, 2327.
54. M. T. Bogert and E. J. Mills, Jr., to E. R. Squibb and Sons, *U.S. pat.* 2,358,786 (1944)—C.A. **39**, 1883.
55. E. K. Bolton to Du Pont Co., *U.S. pat.* 2,402,596 (1946)—C.A. **40**, 5006.
56. F. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 4959-62 (1953)—C.A. **48**, 13624.
57. R. W. Bost and H. C. Schultze, *J. Am. Chem. Soc.*, **64**, 1165-7 (1942)—C.A. **36**, 4106.
58. F. Boutron-Charlard and P. J. Robiquet, *J. de pharm.*, **17**, 294 (1831).
59. K. Brand, *Ber.*, **42**, 3463-8 (1909)—C.A. **4**, 176.
60. H. A. Braun, L. M. Lusky, and H. O. Calvery, *J. Pharmacol.*, **87**, Suppl., 119-25 (1946)—C.A. **41**, 206.
61. George Brecher and S. H. Waxler, *Proc. Soc. Exptl. Biol. Med.*, **70**, 498-501 (1949)—C.A. **43**, 5117.
62. H. Bretschneider and W. Klötzer, *Monatsh.*, **81**, 583-8 (1950)—C.A. **45**, 10215.
63. Herbert Brintzinger, Karl Pfannstiel, Hubert Koddebusch, and K. E. Kling, *Ber.*, **83**, 87-90 (1950)—C.A. **44**, 5308.
64. C. I. Broderick to Boots Pure Drug Co., Ltd., *Brit. pat.* 687,069 (1953)—C.A. **48**, 2765.
65. R. Brown, W. E. Jones, and A. R. Pinder, *J. Chem. Soc.*, **1951**, 2123-5—C.A. **46**, 2486.
66. R. Brown and F. N. Woodward, *J. Chem. Soc.*, **1948**, 42-4—C.A. **42**, 4931.
67. Monamy Buckell, *Nature*, **163**, 330 (1949)—C.A. **43**, 4776.
68. Burroughs Wellcome & Co. (U.S.A.) Inc. to Wellcome Foundation Ltd., *Brit. pat.* 671,926, 671,927 (1952)—C.A. **47**, 5457.
69. A. Bussy, *J. de pharm.*, **26**, 39 (1840); *Ann.*, **34**, 223 (1840).
70. T. Canbäck, *Farm. Rev.*, **45**, 491-2 (1946)—C.A. **40**, 5206.

71. L. Carius, (a) *Ann.*, 122, 71-7; *ibid.*, 124, 221-42 (1862); (b) *ibid.*, 257-64.
72. A. B. Carleton, R. A. Peters, L. A. Stocken, R. H. S. Thompson, and D. I. Williams, *J. Clin. Invest.*, 25, 497-527 (1946)—C.A. 41, 3540.
73. E. Chain, F. J. Philpot, and D. Callow, *Arch. Biochem.*, 18, 171-9 (1948)—C.A. 43, 1455.
74. A. C. Chance and G. A. Levvy, *Quart. J. Exptl. Physiol.*, 34, 79-82 (1947)—C.A. 41, 3528.
75. J. H. Chapman and L. N. Owen, *J. Chem. Soc.*, 1950, 579-85—C.A. 44, 6810.
76. R. G. Charles and Henry Freiser, *J. Am. Chem. Soc.*, 74, 1383-5 (1952)—C.A. 46, 10124.
77. Chem. Fabr. vorm. E. Schering, *Brit. pat.* 265,777 (1926); 293,363 (1927)—C.A. 22, 433; 23, 1724.
78. M. B. Chenoweth, *J. Pharmacol.*, 87, Suppl., 41-54 (1946)—C.A. 41, 204.
79. M. B. Chenoweth, Walter Modell, and W. F. Riker, Jr., *J. Pharmacol.*, 87, Suppl. 6-22 (1946)—C.A. 41, 203.
80. Annette Chesler and R. Tislow, *Science*, 106, 345 (1947)—C.A. 42, 684.
81. Jean Cheymol and Paul Lechat, (a) *Ann. pharm. franc.*, 5, 172-7 (1947); (b) *ibid.*, 262-5—C.A. 42, 680, 997.
82. A. E. Chichibabin, *Fr. pat.* 769,216 (1934)—C.A. 29, 481.
83. A. E. Chichibabin and M. A. Bestuzhev, *Compt. rend.*, 200, 242-4 (1935)—C.A. 29, 2510.
84. Hugo Chiodi and R. A. Sammartino, *Nature*, 160, 680-1 (1947)—C.A. 42, 1666.
85. CIBA Ltd., *Swiss pat.* 265,758 (1950)—C.A. 47, 3869.
86. W. G. Clark and T. A. Geissman, *Nature*, 163, 36-7 (1949); *J. Pharm. Exptl. Therap.*, 95, 362-81 (1949)—C.A. 43, 3104, 5116.
87. L. R. W. Clemence to Abbott Labs., *U.S. pat.* 2,629,724 (1953)—C.A. 48, 737.
88. R. O. Clinton to Sterling Drug Inc., *U.S. pat.* 2,608,574 (1952)—C.A. 47, 5964.
89. R. O. Clinton and U. J. Salvador, *J. Am. Chem. Soc.*, 68, 2076-7 (1946)—C.A. 41, 742.
90. R. O. Clinton, U. J. Salvador, and S. C. Laskowski, *J. Am. Chem. Soc.*, 71, 3366-70 (1949)—C.A. 44, 9375.
91. R. O. Clinton, U. J. Salvador, S. C. Laskowski, and C. M. Suter, *J. Am. Chem. Soc.*, 70, 950-5 (1948)—C.A. 42, 5879.

92. R. O. Clinton, C. M. Suter, S. C. Laskowski, Mary Jackson, and W. Huber, *J. Am. Chem. Soc.*, **67**, 594-7 (1945)—C.A. **39**, 2488.
93. Martino Colonna and R. Andrisano, *Pubbl. ist. chim. univ. Bologna*, **1943**, No. 3, 3-10—C.A. **41**, 754.
94. J. M. Connolly and G. M. Dyson, *J. Chem. Soc.*, **1934**, 822-4—C.A. **28**, 5459.
95. F. G. Covian and J. C. de Oxa, *Bull. Inst. Med. Research, Univ. Madrid*, **1**, 45-52 (1948)—C.A. **43**, 758.
96. H. M. Crooks, Jr., *Chemistry of Penicillin* (H. T. Clarke et al.), **1949**, 455-72—C.A. **44**, 9439.
97. W. W. Crouch and R. T. Werkman to Phillips Pet. Co., U.S. pat. 2,630,448, 2,630,452 (1953)—C.A. **48**, 1431, 1426.
98. C. C. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, **1949**, 278-82—C.A. **43**, 7420.
99. J. F. Danielli, Mary Danielli, J. B. Fraser, P. D. Mitchell, L. N. Owen, and G. Shaw, *Biochem. J.*, **41**, 325-8 (1947)—C.A. **42**, 3859.
100. J. F. Danielli, Mary Danielli, P. D. Mitchell, L. N. Owen, and G. Shaw, *Nature*, **157**, 217-8 (1946)—C.A. **40**, 3823.
101. P. J. Dasher to B. F. Goodrich Co., U.S. pat. 2,304,549, 2,304,550, 2,304,551 (1942)—C.A. **37**, 2960.
102. W. Davies and W. E. Savige, (a) *J. Chem. Soc.*, **1950**, 317-22; (b) *ibid.*, **1951**, 774-9—C.A. **44**, 4867; **45**, 8976.
103. Augusto DeBarbieri and C. Benassi, *Boll. soc. ital. biol. sper.*, **24**, 471-2, 472-4 (1949)—C.A. **43**, 4377.
104. Augusto DeBarbieri and L. Cavalli, *Boll. soc. ital. biol. sper.*, **24**, 475-6 (1949)—C.A. **43**, 4377.
105. Augusto DeBarbieri and Silvia Tricerri, (a) *Boll. soc. ital. biol. sper.*, **24**, 468-9 (1949); (b) *ibid.*, 470-1; (c) *ibid.*, **25**, 522-4 (1949)—C.A. **43**, 4376, 4377; **44**, 8862.
106. Augusto DeBarbieri, F. Vacira, and M. Turri, *Boll. soc. ital. biol. sper.*, **24**, 474-5, 476-7 (1949)—C.A. **43**, 4377.
107. Marcel Delépine and Simon Eschenbrenner, *Bull. soc. chim.*, [4] **33**, 703-11 (1923)—C.A. **17**, 3161.
108. Robert Demuth and Victor Meyer, *Ann.*, **240**, 305-317 (1887).
109. C. W. Denko and A. K. Anderson, *J. Lab. Clin. Med.*, **29**, 1168-76 (1944)—C.A. **39**, 4383.
110. Salvatore DiLauro, *Folio Med. (Naples)*, **32**, 512-8 (1949)—C.A. **44**, 2651.
111. Natale DiMalfetta, *Arch. ist. biochem. ital.*, **11**, 285-94 (1939)—C.A. **34**, 2457.

112. G. L. Dorough to Du Pont Co., U.S. pat. 2,432,296 (1947)—C.A. 42, 5269.
113. E. I. du Pont de Nemours & Co., Brit. pat. 580,357 (1946)—C.A. 21, 2077.
114. S. H. Durlacher, Henry Bunting, H. H. Harrison, N. K. Ordway, and W. S. Albrink, *J. Pharmacol.*, 87, Suppl., 28-32 (1946)—C.A. 41, 204.
115. Pierre Dustin, Jr., *Nature*, 159, 794-7 (1947)—C.A. 41, 5905.
116. Harry Eagle, *Trans. and Studies Coll. Physicians Phil.*, 14, 49-54 (1946)—C.A. 40, 7395.
117. Harry Eagle, F. G. Germuth, Jr., H. J. Magnuson, Ralph Fleischman, Jean C. Grossberg, and Claire E. Tucker, *J. Pharmacol.*, 89, 196-204 (1947)—C.A. 41, 3210.
118. Harry Eagle, H. J. Magnuson, and R. Fleischman, *J. Clin. Invest.*, 25, 451-66 (1946)—C.A. 41, 3539.
119. D. P. Earle, Jr., *Am. J. Physiol.*, 151, 215-20 (1947)—C.A. 42, 1667.
120. N. D. Edge and G. F. Somers, *Quart. J. Pharm. Pharmacol.*, 21, 364-9 (1948)—C.A. 43, 763.
121. H. R. Eisenhauer and K. P. Link, *J. Am. Chem. Soc.*, 76, 1647-9 (1954)—C.A. 49, 6245.
122. E. K. Ellingboe to Du Pont Co., U.S. pat. 2,439,203 (1948)—C.A. 42, 5046.
123. N. Ercoli and William Wilson, *J. Pharmacol. Exptl. Therap.*, 92, 121-6 (1948)—C.A. 42, 3071.
124. Etablissements Poulenc Frères and Carl Oechslin, *Fr. pat.* 643,911 (1927)—C.A. 23, 1649.
125. R. M. Evans, J. B. Fraser, and L. N. Owen, *J. Chem. Soc.*, 1949, 248-55—C.A. 43, 7424.
126. R. M. Evans and L. N. Owen, *J. Chem. Soc.*, 1949, 244-8—C.A. 43, 7423.
127. R. V. G. Ewens and C. S. Gibson, *J. Chem. Soc.*, 1949, 431-5—C.A. 43, 7421.
128. P. Fantl and Margaret H. Nance, *Nature*, 159, 777-8 (1947)—C.A. 41, 6633.
129. Alfred Farah and George Maresh, *J. Pharmacol. Exptl. Therap.*, 92, 73-82 (1948)—C.A. 42, 2674.
130. Farbwerke vorm. Meister, Lucius & Brüning, *Ger. pat.* 202,632 (1907)—C.A. 3, 595.
131. M. W. Farlow to Du Pont Co., U.S. pat. 2,401,234 (1946)—C.A. 40, 5075.

132. M. W. Farlow, Madison Hunt, C. M. Langkammerer, W. A. Lazier, W. J. Peppel, and F. K. Signaigo, *J. Am. Chem. Soc.*, **70**, 1392-4 (1948)—C.A. **42**, 5420.
133. M. W. Farlow and F. K. Signaigo to Du Pont Co., (a) U.S. pat. 2,402,614 (1946); (b) 2,402,615 (1946)—C.A. **40**, 5763, 5760.
134. Fauré, *J. de pharm.*, **17**, 299 (1831).
135. I. Kh. Fel'dman, *Doklady Akad. Nauk. SSSR*, **65**, 857-60 (1949)—C.A. **43**, 6179.
136. Adolf Feldt, Walter Schoeller, and H. G. Allardt to Schering-Kahlbaum, U.S. pat. 2,036,208 (1936)—C.A. **30**, 3593.
137. H. B. Fell and C. B. Allsopp, *Brit. J. Exptl. Path.*, **27**, 310-5 (1946)—C.A. **41**, 2160.
138. O. G. Fitzhugh, Geoffrey Woodward, H. A. Braun, L. M. Lusky, and H. O. Calvery, *J. Pharmacol.*, **87**, Suppl., 23-7 (1946)—C.A. **41**, 203.
139. Zoltán Földi and James Kollonitsch, *J. Chem. Soc.*, **1948**, 1683-5—C.A. **43**, 1722.
140. L. S. Fosdick and H. L. Hansen, *J. Pharmacol.*, **50**, 323-7 (1934)—C.A. **28**, 3798.
141. J. B. Fraser, L. N. Owen, and G. Shaw, *Biochem. J.*, **41**, 328-33 (1947)—C.A. **42**, 4128.
142. Karl Freudenberg and Anton Wolf, *Ber.*, **60**, 232-8 (1927)—C.A. **21**, 1634.
143. E. A. H. Friedheim, U.S. pat. 2,593,434 (1952); *Brit. pat.* 655,435 (1951)—C.A. **46**, 7291; **47**, 144.
144. E. A. H. Friedheim and H. J. Vogel, *Proc. Soc. Exptl. Biol. Med.*, **64**, 418-9 (1947)—C.A. **41**, 4614.
145. K. Fries, *Ann.*, **454**, 121-324 (1927)—C.A. **21**, 2690.
146. K. Fries and G. Schurmann, *Ber.*, **52**, 2170-81 (1919)—C.A. **14**, 2182.
147. Emil Fromm and Heinrich Jörg, *Ber.*, **58**, 304-9 (1925)—C.A. **19**, 1557.
148. Kiyohisa Furukawa, Mototeru Nomura, and Ryohei Oda, *Bull. Inst. Chem. Research, Kyoto Univ.*, **28**, 74 (1952)—C.A. **46**, 11105.
149. S. Gabriel, (a) *Ber.*, **22**, 1137-9 (1889); *ibid.*, **24**, 1110-21 (1891); (b) *ibid.*, **49**, 1110-16 (1916)—C.A. **11**, 807.
150. S. Gabriel and J. Colman, *Ber.*, **45**, 1643-54 (1912)—C.A. **6**, 2618.
151. S. Gabriel and W. E. Lauer, *Ber.*, **23**, 87-96 (1890).
152. S. Gabriel and Ernst Leupold, *Ber.*, **31**, 2832-9 (1898).

153. J. Gadamer, (a) *Arch. Pharm.*, 235, 92 (1897); *Ber.*, 30, 2328, 2330 (1897); (b) *ibid.*, 32, 2338 (1899); *Arch. Pharm.*, 237, 111, 507 (1899).
154. J. F. Gammill, C. M. Southam, and H. B. van Dyke, *Proc. Soc. Exptl. Biol. Med.*, 64, 13-6 (1947)—C.A. 41, 2492.
155. Grace M. Gardner, D. M. Fairley, and W. C. Kuzell, *Proc. Soc. Exptl. Biol. Med.*, 71, 130-1 (1949)—C.A. 43, 7583.
156. J. A. Gardner and Monsanto Chemicals, Ltd., *Brit. pat.* 558,887 (1944)—C.A. 40, 7237.
157. Ludwig Gattermann, *Ber.*, 31, 1136-9 (1898).
158. Erich Gebauer-Fülneegg and Franz V. Meissner, *Monatsh.*, 50, 55-60 (1928)—C.A. 22, 3642.
159. Max Gehrke and Walter Kohler, *Ber.*, 64, 2696-702 (1931)—C.A. 26, 1253.
160. Alfred Gellhorn and H. B. van Dyke, *J. Pharmacol.*, 88, 162-72 (1946)—C.A. 41, 211.
161. F. S. Gerbasi and A. R. Robinson, *Am. J. Clin. Path.*, 19, 668-75 (1949)—C.A. 43, 7587.
162. F. G. Germuth, Jr., and Harry Eagle, *J. Pharmacol. Exptl. Therap.*, 92, 397-410 (1948)—C.A. 42, 4673.
163. D. T. Gibson and Samuel Smiles, *J. Chem. Soc.*, 123, 2388-93 (1923)—C.A. 18, 57.
164. C. S. Gillmor and R. H. Freyberg, *J. Lab. Clin. Med.*, 33, 1024-8 (1948)—C.A. 42, 8951.
165. Alfred Gilman, *Federation Proc.*, 5, 285-92 (1946)—C.A. 40, 5141.
166. Alfred Gilman, R. P. Allen, F. S. Philips, and Ellen St. John, *J. Clin. Invest.*, 25, 549-56 (1946)—C.A. 41, 3540.
167. Alfred Gilman, F. S. Philips, Roberta P. Allen, and Ethol S. Koelle, *J. Pharmacol.*, 87, Suppl., 85-101 (1946)—C.A. 41, 206.
168. Alfred Gilman, F. S. Philips, Ethol S. Koelle, Roberta P. Allen, and Ellen St. John, *Am. J. Physiol.*, 147, 115-26 (1946)—C.A. 41, 219.
169. Henry Gilman and Lawrence Fullhart, *J. Am. Chem. Soc.*, 71, 1478-81 (1949)—C.A. 43, 6574.
170. Henry Gilman and G. C. Gainer, *J. Am. Chem. Soc.*, 71, 1747-51 (1949)—C.A. 43, 8388.
171. Henry Gilman, Mary A. Plunket, L. Tolman, Lawrence Fullhart, and H. S. Broadbent, *J. Am. Chem. Soc.*, 67, 1845-6 (1945)—C.A. 40, 60.

172. Henry Gilman and L. A. Woods, *J. Am. Chem. Soc.*, **67**, 1843-5 (1945)—C.A. **40**, 84.
173. Michael Ginsburg and Miles Weatherall, *Brit. J. Pharmacol.*, **3**, 223-30 (1948); *ibid.*, **4**, 274-6 (1949)—C.A. **43**, 1868; **44**, 751.
174. L. J. Goldsworthy, G. F. Harding, W. L. Norris, S. G. P. Plant, and B. Setton, *J. Chem. Soc.*, **1948**, 2177-9—C.A. **43**, 2928.
175. A. F. Graham, G. A. Levvy, and A. C. Chance, *Biochem. J.*, **41**, 352-7 (1947)—C.A. **42**, 3078.
176. J. D. P. Graham and J. Hood, *Brit. J. Pharmacol.*, **3**, 84-90 (1948)—C.A. **43**, 3100.
177. Giuseppe Graziani, *Folia Med. (Naples)*, **32**, 467-71, 472-3 (1949)—C.A. **44**, 2650.
178. J. D. Gregory and Fritz Lipmann, *J. Am. Chem. Soc.*, **74**, 4017, 4217-18 (1952)—C.A. **47**, 9382.
179. J. D. Gregory, G. D. Novelli, and Fritz Lipmann, *J. Am. Chem. Soc.*, **74**, 854 (1952)—C.A. **47**, 4398.
180. H. Griffon, L. Dérobert, and Clément, *Ann. méd. légale criminol., police sci., méd. sociale et toxicol.*, **28**, 162-4 (1948)—C.A. **43**, 3105.
181. E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 880-91 (1916)—C.A. **11**, 784.
182. C. A. Grob and H. von Sprecher, *Helv. Chim. Acta*, **35**, 885-901 (1952)—C.A. **47**, 5933.
183. D. Grodzenskii, *Farmakol. i Toksikol.*, **9**, No. 3, 54-8 (1946)—C.A. **41**, 5653.
184. Bertil Groth, *Arkiv. Kemi, Mineral. Geol.*, **9**, No. 1, 63 p. (1924)—C.A. **18**, 1280.
185. Martin Gunter and A. C. Ivy, *Proc. Soc. Exptl. Biol. Med.*, **70**, 623-4 (1949)—C.A. **43**, 5118.
186. Ludwig Haitinger, *Monatsh.*, **4**, 165-75 (1884).
187. F. S. Hammett and S. P. Reimann, *J. Exptl. Med.*, **50**, 445-8 (1929)—C.A. **23**, 5479.
188. Carroll A. Handley and Marguerite LaForge, *Proc. Soc. Exptl. Biol. Med.*, **65**, 74-5 (1947)—C.A. **41**, 5626.
189. C. H. G. Hands, A. F. Millidge, and B. Y. Walker, *J. Soc. Chem. Ind.*, **66**, 370 (1947)—C.A. **42**, 1565.
190. Taichi Harada, *Bull. Chem. Soc. Japan*, **6**, 25-8 (1931)—C.A. **25**, 2117.
191. John Harley-Mason, *J. Chem. Soc.*, **1947**, 320-2; **1952**, 146-9—C.A. **41**, 5456; **46**, 9057.

192. S. E. Harris and William Braker to E. R. Squibb & Sons, U.S. pat. 2,342,142 (1944)—C.A. 38, 4758.
193. H. E. Harrison, Henry Bunting, N. K. Ordway, and W. S. Albrink, *J. Ind. Hyg. Toxicol.*, 29, 302-14 (1947)—C.A. 41, 7530.
194. H. E. Harrison, S. H. Durlacher, W. S. Albrink, N. K. Ordway, and Henry Bunting, *J. Pharmacol.*, 87, Suppl., 81-4 (1946)—C.A. 41, 205.
195. H. E. Harrison, N. K. Ordway, S. H. Durlacher, W. S. Albrink, and Henry Bunting, *J. Pharmacol.*, 87, Suppl., 76-80 (1946)—C.A. 41, 205.
196. T. S. Harvey, H. J. Tatum, and Sylvia Himmelfarb, *J. Pharmacol. Exptl. Therap.*, 90, 348-50 (1947)—C.A. 42, 279.
197. P. J. Hawkins and D. S. Tarbell, *J. Am. Chem. Soc.*, 75, 2982-5 (1953)—C.A. 48, 7547.
198. R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 1953, 3219-25—C.A. 48, 12668.
199. Henry and Garot, *J. chem. medicale*, 1, 439, 467 (1825).
200. A. H. Herz and D. S. Tarbell, *J. Am. Chem. Soc.*, 75, 4657-60 (1953)—C.A. 48, 12697.
201. Gerhard Hesse, *Angew. Chem.*, 63, 97 (1951).
202. Gerhard Hesse and Irmgard Jörder, *Ber.*, 85, 924-32 (1952)—C.A. 47, 9975.
203. W. Hieber and R. Brück, *Z. anorg. u. allgem. Chem.*, 269, 13-27 (1952)—C.A. 47, 2623.
204. Philip Hitchcock, *J. Pharmacol.*, 87, Suppl., 55-9 (1946)—C.A. 41, 204.
205. H. H. Hodgson and D. P. Dodgson, (a) *J. Chem. Soc.*, 1948, 870-4; (b) *ibid.*, 1002-4—C.A. 42, 7765; 43, 222.
206. A. W. Hofmann, *Ber.*, 7, 518, 520 (1874); 20, 2251-65 (1887).
207. B. A. Houssay and Carlos Martinez, *Rev. soc. argentina biol.*, 24, 63-72 (1948)—C.A. 43, 5118.
208. O. Hromatka and E. Engel, *Oesterr. Akad. Wiss. Wien. Math.-Naturw. Klasse, Sitzber. Abt. II b*, 157, 29-37, 38-52 (1948)—C.A. 43, 653.
209. Charles Huggins, D. F. Tapley, and E. V. Jensen, *Proc. Natl. Acad. Sci.*, 36, 695-9 (1950)—C.A. 45, 3887.
210. W. F. Hughes, *J. Clin. Invest.*, 25, 541-8 (1946)—C.A. 41, 3540.
211. C. M. Hull, L. A. Weinland, S. R. Olsen, and W. G. France, *Ind. Eng. Chem.*, 40, 513-7 (1948)—C.A. 42, 4788.

212. C. L. Huyck, *Am. Profess. Pharmacist*, 15, 252-3 (1949)—*C.A.* 43, 5492.
213. I. G. Farben., (a) *Brit. pat.* 306,590 (1927); (b) 306,607 (1927); (c) 345,735 (1930); (d) 445,805 (1936); *Fr. pat.* 798,083 (1936)—*C.A.* 23, 5328; 26, 1944; 30, 6766, 7588.
214. I. G. Farben. (Max Bockmühl, Walter Persch, and Walter Kross), *Ger. pat.* 565,064 (1930)—*C.A.* 27, 1093.
215. I. G. Farben. (Richard Herz and Max Schubert), (a) *Ger. pat.* 492,886 (1927); (b) 495,102 (1927)—*C.A.* 24, 2470, 3248.
216. I. G. Farben. (Walter Reppe and Fritz Nicolai), *Ger. pat.* 631,016 (1936)—*C.A.* 30, 6008.
217. *Imp. Chem. Ind.*, (a) *Fr. pat.* 739,500 (1932); (b) *Ger. pat.* 611,144 (1935)—*C.A.* 27, 2163; 29, 4029.
218. *Imp. Chem. Ind., Ltd.*, and C. H. Lumsden, *Brit. pat.* 355,808 (1930)—*C.A.* 26, 5573.
219. *Imp. Chem. Ind.* and K. W. Palmer, (a) *Brit. pat.* 381,237 (1932); (b) 383,284 (1932)—*C.A.* 27, 3946, 4244.
220. H. R. Ing. *J. Chem. Soc.*, 1948, 1393-5—*C.A.* 43, 1321.
221. Harry Irving, E. J. Risdon, and Geoffrey Andrew, *J. Chem. Soc.*, 1949, 537-41—*C.A.* 43, 6107.
222. Kanetsugu Ishii, *J. Japan. Biochem. Soc.*, 24, 118-22 (1952-53)—*C.A.* 47, 12125.
223. Y. Iskander, *J. Chem. Soc.*, 1948, 1549-51—*C.A.* 43, 1753.
224. S. Z. Ivin, *J. Gen. Chem. (USSR)*, 22, 267-9, 327-8 (*Engl. trans.*) (1950)—*C.A.* 46, 10103; 47, 5888.
225. Giovanni Jacini, Tulio Bacchetti, and Luigi Rosnati, *Gaz. chim. ital.*, 82, 297-303 (1952)—*C.A.* 47, 8680.
226. L. O. Jacobson, E. K. Marks, and Evelyn Gaston, *Proc. Soc. Exptl. Biol. Med.*, 69, 84-6 (1948)—*C.A.* 43, 761.
227. P. Jacobson, *Ann.*, 277, 218 (1893).
228. C. B. Jones and D. K. Mecham to Secy. Agr. U.S.A., *U.S. pat.* 2,517,572 (1950)—*C.A.* 44, 10339.
229. S. A. Karjala and S. M. McElvain, *J. Am. Chem. Soc.*, 55, 2966-73 (1933)—*C.A.* 27, 3936.
230. P. Karrer and P. Leiser, *Helv. chim. acta*, 27, 678-84 (1944)—*C.A.* 39, 519.
231. C. Kelber, *Ber.*, 43, 1252-9 (1910)—*C.A.* 4, 2474.
232. C. Kelber and A. Schwarz, *Ber.*, 44, 1693-700 (1911)—*C.A.* 5, 3251.
233. C. J. Kensler and R. W. Elsner, *J. Pharmacol. Exptl. Therap.*, 97, 349-57 (1949)—*C.A.* 44, 1198.

234. M. S. Kharasch and Sidney Weinhouse, U.S. pat. 2,445,356 (1948)—C.A. 42, 8210.
235. A. I. Kiprianov and Z. N. Pazenko, *J. Gen. Chem. (USSR)*, 19, 1523–8, 1529–35 (1949)—C.A. 44, 3487; 45, 3347.
236. A. I. Kiprianov and I. K. Ushenko, *J. Gen. Chem. (USSR)*, 17, 2201–7 (1947)—C.A. 42, 5016.
237. A. I. Kiprianov, I. K. Ushenko, and A. L. Gershun, *J. Gen. Chem. (USSR)*, 14, 865–80 (1944)—C.A. 40, 1829.
238. Morton Klein, J. H. Brewer, J. E. Perez, and Beatrice Day, *J. Immunol.*, 59, 135–40 (1948)—C.A. 42, 5952.
239. Morton Klein and J. E. Perez, *J. Immunol.*, 60, 349–58 (1948)—C.A. 43, 1113.
240. Erwin Klingsberg and Domenick Papa, *J. Am. Chem. Soc.*, 73, 4988–9 (1951)—C.A. 47, 575.
241. T. G. Klumpp and J. B. Rice, *Record of Chem. Progress*, 7, 15–25 (1946)—C.A. 40, 6760.
242. Gerd Kochendoerfer to Deutsche Gold & Silber Scheideanstalt, U.S. pat. 1,753,658 (1930)—C.A. 24, 2471.
243. G. Kögel, *Photo. Ind.*, 29, 126–8 (1931); *Sci. ind. phot.*, [2] 2, 131–2 (1931)—C.A. 26, 5857.
244. A. E. Kretov, A. N. Panchenko, and A. Konovalchik, *J. Gen. Chem. (USSR)*, 1, 390–400 (1931)—C.A. 26, 2442.
245. Stephen Krop, *J. Pharmacol.*, 87, Suppl., 60–5 (1946)—C.A. 41, 205.
246. W. C. Kuzel, P. L. Pillsbury, and S. A. Gellert, *Stanford Med. Bull.*, 5, 197–202 (1947)—C.A. 43, 4765.
247. P. Lafargue, L. P. Doutre, and J. D. Chausse, *J. Med. Bordeaux*, 126, 324–8 (1949)—C.A. 44, 1612.
248. H. P. Lankelma and A. E. Knauf, *J. Am. Chem. Soc.*, 53, 309–12 (1931)—C.A. 25, 931.
249. H. P. Lankelma and Edward Vopicka, *J. Am. Chem. Soc.*, 58, 609–11 (1936)—C.A. 30, 3797.
250. S. C. Laskowski and R. O. Clinton, *J. Am. Chem. Soc.*, 69, 519–21 (1947)—C.A. 41, 4106.
251. Jean de Lattre, *Bull. soc. chim. Belgique*, 26, 323–36 (1912)—C.A. 7, 1361.
252. W. E. Lauer, *Dissertation, Univ. Berlin*, 1889–C. 1890, 899.
253. Arnold Lazarow, *Proc. Soc. Exptl. Biol. Med.*, 66, 4–7 (1947)—C.A. 42, 672.
254. W. A. Lazier and F. K. Signaigo to Du Pont Co., (a) U.S. pat. 2,396,957 (1946); (b) 2,402,640 (1946); (c) 2,402,642 (1946)—C.A. 40, 3935, 5760, 5757.
255. W. A. Lazier, F. K. Signaigo, and J. H. Werntz to Du Pont Co., U.S. pat. 2,402,643 (1946)—C.A. 40, 5764.

256. Rudolf Leuckart, *J. prakt. Chem.*, [2] **41**, 179–224 (1890).
257. A. Leulier and G. Bérnard, (a) *Compt. rend. soc. biol.*, **120**, 651–4 (1935); (b) *ibid.*, **127**, 325–7 (1938)—*C.A.* **30**, 1868; **32**, 3819.
258. A. Leulier, G. Bérnard, and P. Loisy, *J. pharm. chim.*, **25**, 193–216 (1937)—*C.A.* **31**, 7540.
259. A. Leulier and M. Juvin, *J. pharm. chim.*, **14**, 527–31 (1931)—*C.A.* **26**, 3073.
260. A. Leulier, M. Juvin, and H. Tête, *J. pharm. chim.*, **15**, 593–7 (1932)—*C.A.* **26**, 4880.
261. A. Leulier and H. Tête, *J. pharm. chim.*, **17**, 154–60 (1933)—*C.A.* **27**, 3008.
262. A. Leulier, H. Tête, and L. Payre-Ficot, *Assoc. fran. avancement sci.*, **1933**, 432–6; *Ber. ges. Physiol. exptl. Pharmacol.*, **83**, 668—*C.A.* **31**, 3571.
263. Stanley Levey and C. J. Smyth, *J. Lab. Clin. Med.*, **32**, 1364–9 (1947)—*C.A.* **42**, 2019.
264. R. P. Levy, T. W. Moir, and Max Miller, *Proc. Soc. Exptl. Biol. Med.*, **73**, 498–500 (1950)—*C.A.* **44**, 6519.
265. T. R. Lewis and S. Archer, *J. Am. Chem. Soc.*, **73**, 2109–13 (1951)—*C.A.* **46**, 2543.
266. I. M. Lipovich, *J. Applied Chem. (USSR)*, **18**, 718–24 (1945)—*C.A.* **40**, 6407.
267. W. K. Long and A. Farah, *Science*, **104**, 220–1 (1946); *J. Pharmacol.*, **88**, 388–99 (1946)—*C.A.* **40**, 7412; **41**, 1323.
268. W. T. Longcope, *Occupational Med.*, **2**, 34–44 (1946)—*C.A.* **40**, 6715.
269. W. T. Longcope and J. A. Luetscher, *Advances in Internal Med.*, **3**, 1–44 (1949); *Ann. Internal Med.*, **31**, 545–54 (1949)—*C.A.* **43**, 8408; **44**, 229.
270. W. T. Longcope, J. A. Luetscher, E. Calkins, D. Grob, S. W. Bush, and H. Eisenberg, *J. Clin. Invest.*, **25**, 557–67 (1946)—*C.A.* **41**, 3541.
271. W. T. Longcope, J. A. Luetscher, M. M. Wintrobe, and V. Jager, *J. Clin. Invest.*, **25**, 528–33 (1946)—*C.A.* **41**, 3540.
272. J. D. Loudon and Nathan Shulman, *J. Chem. Soc.*, **1939**, 1066–7—*C.A.* **33**, 6793.
273. J. A. Luetscher, Harry Eagle, and W. T. Longcope, *J. Clin. Invest.*, **25**, 534–40 (1946)—*C.A.* **41**, 3540.
274. Auguste Lumière, (a) *Compt. rend.*, **176**, 540–1 (1923); (b) *Bull. sci. pharmacol.*, **41**, 129–36 (1934)—*C.A.* **17**, 1978; **28**, 3840.

275. Auguste Lumière and A. Léonet, *Presse. méd.*, **48**, 1017–8 (1940)—C.A. **37**, 3503.
276. Auguste Lumière and Felix Perrin, (a) 14 me. Cong. chim. ind. Paris, 1934, 3 p.; (b) *Compt. rend.*, **184**, 289–91 (1927)—C.A. **29**, 5990; **22**, 1015.
277. L. M. Lusky, H. A. Braun, and E. P. Lang, *J. Ind. Hyg. Toxicol.*, **31**, 301–5 (1949)—C.A. **44**, 2643.
278. L. M. Lusky, H. A. Braun, and Geoffrey Woodward, *Cancer Research*, **7**, 667–81 (1947)—C.A. **42**, 8324.
279. Eugenia S. de Lustig, Hugo Chiodi, and Teofilo P. Ressia, *Rev. soc. argentina biol.*, **24**, 35–43 (1948)—C.A. **42**, 8335.
280. Feodor Lynen and Ernestine Reichert, *Angew. Chem.*, **63**, 47–8 (1951)—C.A. **45**, 3881.
281. Feodor Lynen, Ernestine Reichert, and Luistraud Rueff, *Ann.*, **574**, 1–32 (1951)—C.A. **46**, 11327.
282. R. A. McCance and E. M. Widdowson, *Nature*, **157**, 837 (1946)—C.A. **40**, 6171.
283. E. W. McClelland, *J. Chem. Soc.*, 1929, 1588–93—C.A. **23**, 4700.
284. H. McCombie and B. C. Saunders, *Nature*, **158**, 382–5 (1946)—C.A. **41**, 2807.
285. F. F. McDonald, *Brit. J. Pharmacol.*, **3**, 116–7 (1948)—C.A. **42**, 7445.
286. I. W. McDonald, *Nature*, **157**, 837 (1946)—C.A. **40**, 6171.
287. W. de B. MacNider, (a) *Proc. Soc. Exptl. Biol. Med.*, **66**, 444–6 (1947); (b) *Proc. Soc. Exptl. Med.*, **62**, 160–1 (1948)—C.A. **42**, 2352, 6936.
288. W. de B. MacNider, J. C. Trott, Jr., and Margaret D. Bruce, *J. Pharmacol. Exptl. Therap.*, **94**, 262–73 (1948)—C.A. **43**, 1110.
289. V. E. Maevskii and O. I. Fetisova, *Farmakol. i Toksikol.*, **7**, No. 4, 39–44 (1944)—C.A. **39**, 3592.
290. Sverrir Magnusson, J. E. Christian, and G. L. Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **36**, 257–60 (1947)—C.A. **42**, 877.
291. M. S. Malinovskii and B. N. Moryganov, *Priklad. Khim.*, **21**, 995–1001 (1948)—C.A. **43**, 1391.
292. Manchester Oxide Co. Ltd., J. H. Clayton, and Bernard Bann, *Brit. pat.* 546,277, 546,278, 546,279 (1942)—C.A. **37**, 3104.
293. I. Mann, A. Pirie, and D. B. Pullinger, *Am. J. Ophthalmol.*, **30**, 421–35 (1947)—C.A. **43**, 4372.
294. H. M. Margolis and P. S. Kaplan, *Ann. Internal Med.*, **27**, 353–60 (1947)—C.A. **42**, 285.

295. Carlos Martinez, *Rev. asoc. méd. argentina*, *64*, 127-9 (1950)—C.A. *44*, 6949.
296. Simao Mathias, *Bols. Faculdade filosofia, cienc. letras, Univ. Sao Paulo*, *14*, *Quimica* No. 1, 75-140 (1942)—C.A. *40*, 2792.
297. E. M. Meade and F. N. Woodward, *J. Chem. Soc.*, *1948*, 1894-5—C.A. *43*, 2935.
298. J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, *56*, 2177-80 (1934)—C.A. *29*, 797.
299. L. W. C. Miles and L. N. Owen, (a) *J. Chem. Soc.*, *1950*, 2934-8; (b) *ibid.*, 2938-43; (c) *ibid.*, 2943-6; (d) *ibid.*, *1952*, 817-26—C.A. *45*, 6156, 6157, 6158; *47*, 1070.
300. E. J. Mills, Jr., and M. T. Bogert, *J. Am. Chem. Soc.*, *62*, 1173-80 (1940)—C.A. *34*, 6284.
301. Walter Modell, M. B. Chenoweth, and Stephen Krop, *J. Pharmacol.*, *87*, *Suppl.*, 33-40 (1946)—C.A. *41*, 204.
302. Walter Modell, H. Gold, and McKeen Cattell, *J. Clin. Invest.*, *25*, 480-7 (1946)—C.A. *41*, 3540.
303. J. C. Mondragón R., *Rev. facultad farm. y bioquim., Univ. nacl. mayor San Marcos (Lima, Peru)*, *11*, 183-95 (1949)—C.A. *45*, 548.
304. E. E. Moore to Abbott Labs., U.S. pat. 2,509,198 (1950)—C.A. *44*, 9478.
305. A. L. Morrison and K. J. M. Andrews to Roche Prods. Ltd., *Brit. pat.* 690,576 (1953)—C.A. *48*, 7046.
306. Werner Mylius, *Ber.*, *49*, 1091-101 (1916)—C.A. *11*, 805.
307. Takio Naito, *J. Pharm. Soc. Japan*, *64*, 133-4 (1944)—C.A. *45*, 2918.
308. A. H. Nathan and M. T. Bogert, *J. Am. Chem. Soc.*, *63*, 2361-6 (1941)—C.A. *35*, 7407.
309. C. D. Nenitzescu and Nicolae Scarlatescu, *Ber.*, *68*, 587-91 (1935)—C.A. *29*, 3979.
310. W. F. Neuman and R. P. Allen, *J. Pharmacol. Exptl. Therap.*, *96*, 95-8 (1949)—C.A. *43*, 6309.
311. Ya. Kh. Nolle, *Farm. i. Farmakol. (USSR)*, *1937*, No. 2, 1-8—C.A. *34*, 3820.
312. N. V. Bataafsche, (a) *Brit. pat.* 508,932 (1939); (b) 532,676 (1941)—C.A. *34*, 2863; *36*, 1045.
313. Paul Nylén and Arvid Olsen, *Svensk Kem. Tid.*, *53*, 274-81 (1941)—C.A. *36*, 753.
314. Ryohei Oda, *Mem. Fac. Eng. Kyoto Univ.*, *14*, 195-205 (1952)—C.A. *48*, 1935.
315. Heinz Ohle, Willi Mertens, M. Andrée, and E. Euler, *Ber.*, *68*, 2176-87 (1935)—C.A. *30*, 2178.

316. Masaki Ohta, *J. Pharm. Soc. Japan*, **70**, 709–11 (1950)—*C.A.* **45**, 6581.
317. C. T. Olcott and W. F. Riker, Jr., *Science*, **105**, 67 (1947)—*C.A.* **42**, 8347.
318. H. S. Olcott, *Science*, **96**, 454 (1942)—*C.A.* **37**, 2407.
319. J. F. Olin and F. B. Dains, *J. Am. Chem. Soc.*, **52**, 3322–7 (1930)—*C.A.* **24**, 4766.
320. Jan Opplt, U.S. pat. 2,585,580 (1952)—*C.A.* **46**, 5270.
321. G. Ottaviano and G. Previtera, *Boll. soc. ital. biol. sper.*, **26**, 967–8 (1950)—*C.A.* **46**, 5124.
322. I. H. Page and Arda A. Green, *Am. J. Physiol.*, **156**, 405–11 (1949)—*C.A.* **43**, 6320.
323. K. W. Palmer to Imp. Chem. Ind., (a) U.S. pat. 1,968,905, 1,968,906 (1934); (b) 2,004,728 (1935)—*C.A.* **28**, 6158; **29**, 5127.
324. W. E. Parham, *J. Am. Chem. Soc.*, **69**, 2449–51 (1947)—*C.A.* **42**, 1287.
325. W. E. Parham, Hans Wynberg, and F. L. Ramp, *J. Am. Chem. Soc.*, **75**, 2065–9 (1953)—*C.A.* **48**, 4548.
326. Parke, Davis & Co., *Brit. pat.* 712,065 (1954)—*C.A.* **48**, 13714.
327. J. C. Patrick to Thiokol Corp., (a) U.S. pat. 2,479,542 (1949); (b) 2,527,377 (1950)—*C.A.* **44**, 5377; **45**, 391.
328. J. C. Patrick and H. R. Ferguson to Thiokol Corp., U.S. pat. 2,527,374 (1950)—*C.A.* **45**, 390.
329. A. A. Pavlic to Du Pont Co., U.S. pat. 2,408,094 (1946)—*C.A.* **41**, 775.
330. A. A. Pavlic, W. A. Lazier, and F. K. Signaigo, *J. Org. Chem.*, **14**, 59–64 (1949)—*C.A.* **43**, 3783.
331. A. A. Pavlic and W. J. Peppel to Sec'y of War U.S.A., U.S. pat. 2,397,689 (1946)—*C.A.* **40**, 4077.
332. W. J. Peppel and F. K. Signaigo to Du Pont Co., U.S. pat. 2,402,665 (1946)—*C.A.* **40**, 5762.
333. J. E. Perez, Josefina Baralt-Perez, and Morton Klein, *J. Immunol.*, **62**, 405–13 (1949)—*C.A.* **43**, 8551.
334. R. A. Peters, G. H. Spray, L. A. Stocken, C. H. Collie, M. A. Grace, and G. A. Wheatley, *Biochem. J.*, **41**, 370–3 (1947)—*C.A.* **42**, 3078.
335. R. A. Peters, L. A. Stocken, and R. H. S. Thompson, *Nature*, **156**, 616–9 (1945)—*C.A.* **40**, 1614.
336. R. A. Peters, L. A. Stocken, R. H. S. Thompson, F. N. Woodward, A. F. Millidge, and E. J. Gasson, U.S. pat. 2,432,797 (1947)—*C.A.* **42**, 2623.

337. R. A. Peters, R. W. Wakelin, and R. Cecil, *Biochem. J.*, **43**, 45–51 (1948)—C.A. **43**, 2254.
338. J. S. Philpot, *Brit. pat.* 594,008 (1947)—C.A. **42**, 2986.
339. P. Pichat, *Compt. rend. soc. biol.*, **132**, 13–4 (1939)—C.A. **34**, 587.
340. M. Picon, *J. pharm. chim.*, **21**, 215–25 (1935)—C.A. **29**, 7500.
341. Jakob Pollak and Eugen Riesz, *Monatsh.*, **50**, 251–62 (1928); *ibid.*, **53/54**, 90–9 (1929)—C.A. **23**, 825; **24**, 351.
342. E. Praetorius, *Biochim et Biophys. Acta*, **2**, 590–601 (1948)—C.A. **43**, 3865.
343. J. D. Pratt, R. A. Peters, L. A. Stocken, and R. H. S. Thompson, *Brit. pat.* 579,971 (1946)—C.A. **41**, 2077.
344. E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovskii, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, **1951**, 438–47, 560–7; *ibid.*, **1952**, 478–83; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **1952**, 459–63 (Engl. trans.)—C.A. **46**, 3494, 7044; **47**, 4840; **48**, 5074.
345. E. N. Prilezhaeva, M. F. Shostakovskii, and E. S. Shapiro, *Akad. Nauk SSSR, Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, **2**, 171–3 (1952)—C.A. **48**, 552.
346. Vittorio Puccinelli, *Rass. med. (Milan)*, **25**, 121–36 (1948)—C.A. **43**, 6761.
347. A. N. Pudovik and N. N. Kudryavtseva, *J. Gen. Chem. (USSR)*, **20**, 848–54 (1950)—C.A. **44**, 9338.
348. R. V. Randall and A. O. Seeler, *New Engl. J. Med.*, **239**, 1004–9, 1040–6 (1948)—C.A. **43**, 1882.
349. A. L. Raymond, *Advances in Carbohydrate Chemistry*, **1**, 129–45 (1945)—C.A. **40**, 4679.
350. Reboul, *Ann. chim. phys.*, [3] **60**, 65–7 (1860)—*Ann.*, *Supl. 1*, 240 (1861).
351. T. A. Redonnet, *Med. españ.*, **19**, 327–8 (1948)—C.A. **42**, 7871.
352. A. M. Reeves and E. E. Reid, Paper read at Organic Division, Am. Chem. Soc., San Francisco, March 1949.
353. E. E. Reid—Personal observation.
354. S. P. Reimann and F. S. Hammett, *Proc. Soc. Exptl. Biol. Med.*, **27**, 20–2 (1929)—C.A. **24**, 5310.
355. Arnold Reissert and Karl Crämer, *Ber.*, **61**, 2555–66 (1928)—C.A. **23**, 2163.
356. H. Rennert, *Ber.*, **48**, 549–70 (1915)—C.A. **9**, 1774.
357. R. R. Renshaw, P. F. Dreisbach, M. Ziff, and D. Green, *J. Am. Chem. Soc.*, **60**, 1765–70 (1938)—C.A. **32**, 7412.

358. Walter Reppe and Adolf Freytag, Ger. pat. 696,774 (1940)—C.A. 35, 5909.
359. Walter Reppe and Fritz Nicolai to I. G. Farben., U.S. pat. 2,105,845 (1937)—C.A. 32, 2372.
360. Heinrich Rheinboldt, Ernesto Giesbrecht, and Simao Mathias, Univ. Sao Paulo, Faculdade filosof., cienc e letras, Bol. No. 129, Quimica, No. 3, 133-9 (1951)—C.A. 46, 7554.
361. Heinrich Rheinboldt and Christian Tetsch, Ber., 70, 675-80 (1937)—C.A. 31, 4270.
362. D. A. Richert and A. D. Bass, J. Pharmacol. Exptl. Therap., 95, 92-4 (1949)—C.A. 43, 2700.
363. N. K. Richtmyer, C. J. Carr, and C. S. Hudson, J. Am. Chem. Soc., 65, 1477-8 (1943)—C.A. 37, 5698.
364. Eugen Riesz and Walter Frankfurter, Monatsh., 50, 68-75 (1928)—C.A. 22, 3644.
365. G. W. Rigby to Du Pont Co., U.S. pat. 2,423,344 (1947)—C.A. 41, 6277.
366. W. F. Riker, Jr., J. Pharmacol., 87, Suppl., 66-71 (1946)—C.A. 41, 205.
367. W. F. Riker, Jr., and George Rosenfeld, J. Pharmacol., 87, Suppl., 72-5 (1946)—C.A. 41, 205.
368. J. M. Robson and J. A. Nissim, Chem. Products, 11, 163-7 (1948)—C.A. 43, 7144.
369. C. A. Rojahn and Gustav Lemme, Arch. Pharm., 263, 612-24 (1925)—C.A. 20, 737.
370. J. Roos, Ber., 21, 619-30 (1888).
371. Raphael Rosen and E. E. Reid, J. Am. Chem. Soc., 44, 634-6 (1922)—C.A. 16, 1559.
372. W. C. J. Ross, J. Chem. Soc., 1950, 815-8—C.A. 44, 6838.
373. Rozier and Jullien, Bull. sci pharmacol., 41, 149-52 (1934)—C.A. 28, 4130.
374. T. Ruemele and G. T. Walker, Soap, Perfumery & Cosmetics, 26, 461-2 (1953)—C.A. 47, 10178.
375. Brian Russell, Bernard Green, and L. G. R. Ward, Lancet, 255, 169-74 (1948)—C.A. 42, 8968.
376. H. W. Ryder, Jacob Cholak, and R. B. Kehoe, Science, 106, 63-4 (1947)—C.A. 41, 6333.
377. L. R. Rykhan and C. L. A. Schmidt, Univ. Calif. Pub. Physiol., 8, 257-76 (1944)—C.A. 38, 2977.
378. S. N. Sarkar, Nature, 162, 265-6 (1948)—C.A. 43, 361.
379. Kiyoo Sato and Katashi Makino, Nature, 167, 238 (1951)—C.A. 45, 8982.

380. J. L. Sawyers, Benjamin Burrows, and T. H. Maren, *Proc. Soc. Exptl. Biol. Med.*, 70, 194-7 (1949)—C.A. 43, 3931.
381. Schering-Kahlbaum, (a) *Brit. pat.* 373,755 (1932); (b) 454,244 (1936); (c) 386,562, 397,293, 398,020 (1933)—C.A. 27, 3946; 31, 1164; 27, 4350; 28, 859, 1140.
382. Schering-Kahlbaum (H. G. Allardt), *Ger. pat.* 575,598 (1933)—C.A. 27, 4880.
383. Schering-Kahlbaum (Adolf Feldt, Walter Schoeller, and Erich Borgwardt), *Ger. pat.* 513,799 (1926)—C.A. 25, 1640.
384. Schering-Kahlbaum (Victor Fischl, Adolf Feldt, and Erwin Schwenk), *Ger. pat.* 645,726 (1937)—C.A. 31, 6416.
385. Schering-Kahlbaum (Walter Schoeller and H. G. Allardt), *Ger. pat.* 527,036 (1926)—C.A. 25, 4664.
386. Schering-Kahlbaum, A.-G. (Walter Schoeller, Adolf Feldt, and H. G. Allardt), *Ger. pat.* 573,629 (1933); 625,995 (1936)—C.A. 27, 4349; 30, 5728.
387. Schering-Kahlbaum (Erwin Schwenk and Max Gherke), *Ger. pat.* 557,247 (1930)—C.A. 27, 374.
388. Wilhelm Schneider, (a) *Ber.*, 41, 4466-70 (1908); *ibid.*, 42, 3416-20 (1909); *Ann.*, 375, 207-54 (1910); (b) *Ber.*, 45, 2961-5 (1912); (c) *ibid.*, 49, 1638-43 (1916)—C.A. 3, 658; 4, 173, 3064; 7, 1006; 11, 1967.
389. Wilhelm Schneider and August Bansa, *Ber.*, 66, 1973-5 (1933)—C.A. 28, 1024.
390. Wilhelm Schneider and Annemarie Beuther, *Ber.*, 52, 2135-49 (1919)—C.A. 14, 2178.
391. W. Schneider and D. Clibbens, *Ber.*, 47, 2218-24 (1914) C.A. 8, 3057.
392. Wilhelm Schneider, Douglas Clibbens, Gustav Hullweck, and Werner Steibelt, *Ber.*, 47, 1258-69 (1914)—C.A. 8, 2388.
393. Wilhelm Schneider, Hellmuth Fischer, and Walter Specht, *Ber.*, 63, 2787-98 (1930)—C.A. 25, 1833.
394. Wilhelm Schneider, Rudolf Gille, and Kurt Eisfeld, *Ber.*, 61, 1244-59 (1928)—C.A. 22, 4107.
395. Wilhelm Schneider and Herbert Leonhardt, *Ber.*, 62, 1384-9 (1929)—C.A. 23, 4932.
396. Wilhelm Schneider and Wilhelm Lohmann, *Ber.*, 45, 2954-61 (1912)—C.A. 7, 1005.
397. Wilhelm Schneider and L. A. Schütz, *Ber.*, 46, 2634-40 (1913)—C.A. 8, 97.

398. Wilhelm Schneider and Otilie Stiehler, *Ber.*, 52, 2131-5 (1919)—C.A. 14, 2178.
399. Wilhelm Schneider and Fritz Wrede, *Ber.*, 47, 2225-9 (1914)—C.A. 8, 3057.
400. Walter Schoeller and H. G. Allardt, U.S. pat. 1,683,105 (1928)—C.A. 22, 3959.
401. Walter Schoeller, Erich Borgwardt, and Adolf Feldt to Chem. Fabr. Actien vorm. E. Schering, U.S. pat. 1,784,497 (1930)—C.A. 25, 969.
402. Alexander Schönberg and Youssef Iskander, *J. Chem. Soc.*, 1942, 90-5—C.A. 36, 3495.
403. Lennart Schotte, *Acta Chem. Scand.*, 4, 1304-5 (1950); *Arkiv Kemi*, 3, 397-404 (1951); *ibid.*, 5, 533-42 (1953)—C.A. 46, 6594, 6595; 48, 9321.
404. Maxwell Schubert, Evelyn Goldberg, and Freda G. Schreiber, *Am. J. Trop. Med.*, 29, 115-27 (1949)—C.A. 43, 9266.
405. G. Schwarzenbach and H. Egli, *Helv. chim. acta*, 17, 1176-82 (1934)—C.A. 29, 1077.
406. G. Schwarzenbach and E. Rudin, *Helv. chim. acta*, 22, 360-76 (1939)—C.A. 33, 6266.
407. Erwin Schwenk and Max Gehrke to Schering-Kahlbaum, U.S. pat. 2,038,609 (1936)—C.A. 30, 3947.
408. Otto Seitz, *Ber.*, 24, 2624-31 (1891).
409. M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1951, 284-94, 1954, 292-302, 303-13; *Akad. Nauk SSSR, Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik*, 2, 174-8 (1952)—C.A. 46, 883; 48, 10535, 552.
410. F. K. Signaigo to DuPont Co., (a) U.S. pat. 2,402,456 (1946); (b) 2,440,729 (1948)—C.A. 40, 5767; 42, 5923.
411. F. K. Signaigo to Sec'y of War U.S.A., U.S. pat. 2,467,602 (1949)—C.A. 43, 6223.
412. F. K. Signaigo and W. J. Peppel to DuPont Co., U.S. pat. 2,410,844 (1946)—C.A. 41, 344.
413. S. D. Simpson, *Can. J. Res.*, 25B, 20-7 (1947)—C.A. 41, 3051.
414. Bertil Sjöberg, (a) *Svensk Kem. Tid.*, 50, 250-4 (1938); (b) *Ber.*, 74, 64-72 (1941); (c) *ibid.*, 75, 13-29 (1942); (d) *Z. physik. Chem.*, 52B, 209-21 (1942)—C.A. 33, 2106; 35, 5092; 36, 6138; 37, 6191.
415. K. H. Slotta and R. Tschesche, *Ber.*, 62, 1398-1405 (1929)—C.A. 23, 4931.

416. Lennart Smith and Bertil Sjöberg, *Ber.*, 69, 678–80 (1936)—C.A. 30, 4465.
417. H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol.*, 26, 269–73 (1944)—C.A. 39, 136.
418. C. V. Smythe, *J. Biol. Chem.*, 114, 601–12 (1936)—C.A. 30, 6399.
419. E. E. Snell, G. M. Brown, V. J. Peters, Jean A. Craig, E. L. Wittle, J. A. Moore, W. M. McGlohon, and O. D. Bird, *J. Am. Chem. Soc.*, 72, 5349–50 (1950)—C.A. 45, 3021.
420. E. E. Snell, E. L. Wittle, and J. A. Moore to Parke, Davis & Co., U.S. pat. 2,625,565 (1953)—C.A. 48, 1431.
421. H. R. Snyder and J. M. Stewart to Phillips Pet. Co., (a) U.S. pat. 2,497,100 (1950); (b) 2,505,870 (1950); (c) 2,620,328 (1952)—C.A. 44, 4025, 7352; 47, 3025.
422. H. R. Snyder, J. M. Stewart, and J. B. Ziegler, (a) *J. Am. Chem. Soc.*, 69, 2672–4 (1947); (b) *ibid.*, 2675–7—C.A. 42, 1881, 1882.
423. Soc. belge de l'azote et des produits chimiques du Marly S. A., Belg. pat. 507,623, 513,023, 513,287 (1952), 515,060 (1953)—C.A. 48, 2333, 2334.
424. Soc. chim. à Bâle, (a) Swiss pat. 210,960 (1940); (b) 210,962 (1940)—C.A. 36, 3591, 2649.
425. Walter Specht, *Zur Kenntnis des Sinalbins und der Thio-glucose*, Jena, 1931, 43 p.
426. G. H. Spray, (a) *Biochem. J.*, 41, 360–1 (1947); (b) *ibid.*, 366–70—C.A. 42, 3014, 3078.
427. G. H. Spray, L. A. Stocken, and R. H. S. Thompson, *Biochem. J.*, 41, 362–6 (1947)—C.A. 42, 3078.
428. Norbert Steiger to Hoffmann-LaRoche Inc., U.S. pat. 2,454,260 (1948)—C.A. 43, 1438.
429. Norbert Steiger to Roche Products Ltd., Brit. pat. 637,130 (1950)—C.A. 44, 8380.
430. D. S. Stevenson, R. M. Suarez, Jr., and E. J. Marchand, *Puerto Rico J. Pub. Health, Trop. Med.*, 43, 533–53 (1948) C.A. 43, 3523.
431. J. M. Stewart, (a) *Proc. Montana Acad. Sci.*, 7–8, 83–4 (1947–8); (b) Abstracts of Papers Presented at the 115th Meeting of the A.C.S., San Francisco, Calif., Apr., 1949, p. 69L.—C.A. 45, 2852.
432. J. M. Stewart and H. P. Cordts, *J. Am. Chem. Soc.*, 74, 5880–4 (1952)—C.A. 48, 1263.
433. L. A. Stocken, (a) *J. Chem. Soc.*, 1947, 592–5; (b) *Biochem. J.*, 41, 358–60 (1947)—C.A. 41, 6197; 42, 3078.

434. L. A. Stocken and R. H. S. Thompson, (a) *Biochem. J.*, **40**, 535-48, 548-54 (1946); (b) *ibid.*, 529-35; *Physiol. Revs.*, **29**, 168-94 (1949)—C.A. **41**, 215; **43**, 6739.
435. L. A. Stocken, R. H. S. Thompson, and V. P. Whittaker, *Biochem. J.*, **41**, 47-51 (1947)—C.A. **41**, 4578.
436. I. D. E. Storey, G. A. Levvy, and A. C. Chance, *J. Clin. Invest.*, **25**, 497-527 (1946)—C.A. **41**, 3540.
437. M. X. Sullivan and W. C. Hess, *U.S. Pub. Health Repts.*, **44**, 1599-1608 (1929)—C.A. **23**, 4445.
438. M. B. Sulzberger, R. L. Baer, and A. Kanof, *J. Clin. Invest.*, **25**, 474-9, 488-96 (1946)—C.A. **41**, 3540.
439. C. G. Sundt, *Tids. Norske Laegeforen.*, **67**, 356-8 (1948)—C.A. **43**, 1104.
440. R. M. Sussman and J. A. Schack, *Proc. Soc. Exptl. Biol. Med.*, **66**, 247-8 (1947)—C.A. **42**, 1660.
441. C. M. Suter and H. L. Hansen, *J. Am. Chem. Soc.*, **54**, 4100-4104 (1932)—C.A. **26**, 5926.
442. L. E. Sutton, *J. Am. Med. Assoc.*, **104**, 2168-71 (1935)—C.A. **29**, 6650.
443. L. E. Sutton to Chemical Foundation, U.S. pat. 1,926,797 (1933)—C.A. **27**, 5895.
444. Tomoji Suzuki, Kazuo Imaeda, Mitsuji Kubota, and Hiroshi Takagi, *Japan. J. Pharm. & Chem.*, **22**, 464-6 (1950)—C.A. **45**, 8458.
445. L. C. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, **52**, 651-60 (1930)—C.A. **24**, 1341.
446. Ladislaus von Szathmary, *Ber.*, **43**, 2485-7 (1910)—C.A. **4**, 3232.
447. F. Taboury, *Bull. soc. chim.*, [3] **33**, 836-9 (1905); *ibid.*, **35**, 668-74 (1906).
448. Wadie Tadros and Ezzat Saad, *J. Chem. Soc.*, **1954**, 1155-6—C.A. **49**, 3878.
449. Torizo Takahashi and Harno Saikachi, *J. Pharm. Soc. Japan*, **62**, 140-3 (1942)—C.A. **45**, 1592.
450. Torizo Takahashi, Shin-ichi Shimamura, Shuzo Shimada, and Hiroshi Hayase, *J. Pharm. Soc. Japan*, **65**, No. 5-6A, 10-11 (1945)—C.A. **45**, 8530.
451. D. S. Tarbell and A. H. Herz, *J. Am. Chem. Soc.*, **75**, 1668-73 (1953)—C.A. **48**, 4468.
452. B. Tchoubar and Letellier-Dupré, *Bull. soc. chim.*, **1947**, 792-4—C.A. **42**, 1564.
453. J. G. Telfer, *J. Am. Med. Assoc.*, **135**, 835-7 (1947)—C.A. **42**, 3077.

454. Helen M. Tepperman, *J. Pharmacol.*, **89**, 343-9 (1947)—*C.A.* **41**, 4234.
455. Christian Tetsch, Thesis, Friedrich Wilhelm Univ., Bonn, 1935.
456. C. H. Thienes, *Calif. Med.*, **67**, 90-4 (1947)—*C.A.* **41**, 7513.
457. K. V. Thimann and W. D. Bonner, Jr., *Am. J. Botany*, **36**, 214-21 (1949); *Proc. Natl. Acad. Sci. U.S.*, **35**, 272-6 (1949)—*C.A.* **43**, 5094, 8462.
458. J. R. Thirtle, *J. Am. Chem. Soc.*, **68**, 342-3 (1946)—*C.A.* **40**, 2148.
459. Lewis Thomas and C. A. Stetson, Jr., *Bull. Johns Hopkins Hosp.*, **83**, 176-80 (1948)—*C.A.* **42**, 8972.
460. H. W. Thompson, *J. Am. Chem. Soc.*, **61**, 1396-1400 (1939)—*C.A.* **33**, 6156.
461. J. F. Thompson, Joseph Savit, and Eugene Goldwasser, *J. Pharmacol.*, **89**, 1-13 (1947)—*C.A.* **41**, 3208.
462. R. H. S. Thompson and V. P. Whittaker, *Biochem. J.*, **41**, 342-6 (1947)—*C.A.* **42**, 3077.
463. J. M. Thorp, Botha de Meillon, and F. Hardy, *S. African J. Med. Sci.*, **13**, 151-8 (1948)—*C.A.* **43**, 4772.
464. J. M. Tobias, C. C. Lushbaugh, H. M. Patt, S. Postel, M. N. Swift, and R. W. Gerard, *J. Pharmacol.*, **87**, Suppl., 102-18 (1946)—*C.A.* **41**, 206.
465. Masao Tomita and Hiroshi Yamada, *J. Pharm. Soc. Japan*, **68**, 149-50 (1948)—*C.A.* **48**, 3920.
466. Masao Tomita, Hiroshi Yamada, and Keiichiro Hozumi, *J. Pharm. Soc. Japan*, **69**, 403-4 (1949)—*C.A.* **44**, 1922.
467. Heou-Feo Tseou and Tsu-Ling Pan, *J. Chinese Chem. Soc.*, **7**, 29-32 (1939)—*C.A.* **34**, 1970.
468. E. E. Van Tamelen, *J. Am. Chem. Soc.*, **73**, 3444-8 (1951)—*C.A.* **46**, 4492.
469. W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472-6 (1942); U.S. pat. 2,398,480 (1946)—*C.A.* **37**, 1083; **40**, 3766.
470. W. E. Vaughan and F. F. Rust to Shell Dev. Co., U.S. pat. 2,398,479 (1946); Brit. pat. 558,790 (1944)—*C.A.* **40**, 3765; **41**, 150.
471. Z. J. Vejdelek and Miroslav Protiva, *Chem. Listy*, **45**, 451-2 (1951)—*C.A.* **47**, 8068.
472. W. H. Vinton to Du Pont Co., U.S. pat. 2,427,582 (1947); 2,607,776 (1952)—*C.A.* **42**, 212; **47**, 6989.

473. Anton von Wacek and H. O. Eppinger, *Ber.*, **73**, 644–51 (1940)—C.A. **35**, 2874.
474. Anton von Wacek, H. O. Eppinger, and André von Bézard, *Ber.*, **73**, 521–31 (1940)—C.A. **34**, 6617.
475. P. Wagner, *Chem. Ztg.*, **32**, 76–7 (1908)—C.A. **2**, 1147.
476. L. L. Waters and Chester Stock, *Science*, **102**, 601–6 (1945)—C.A. **40**, 1251.
477. E. R. Watson and S. B. Dutt, *J. Chem. Soc.*, **121**, 2414–9 (1922); *J. and Proc. Asiatic Soc. Bengal*, **18**, No. 6. (*Proc. 9th Indian Sci. Cong.*), lxx–lxxi (1922)—C.A. **17**, 546; **18**, 1487.
478. M. Weatherall, (a) *Brit. J. Pharmacol.*, **3**, 137–45 (1948); (b) *J. Pharm. Pharmacol.*, **1**, 576–92 (1949)—C.A. **42**, 7446; **43**, 9250.
479. E. C. Webb and Ruth van Heyingen, *Biochem. J.*, **41**, 74–8 (1947)—C.A. **41**, 4523.
480. H. Weil-Malherbe, *Ann. Rev. Biochem.*, **17**, 1–34 (1948)—C.A. **42**, 8839.
481. Wellcome Foundation, Ltd. (G. H. Hitchings and P. B. Russell), *Ger. pat.* 831,994 (1952)—C.A. **48**, 10776.
482. F. W. Wenzel, Jr., and E. E. Reid, *J. Am. Chem. Soc.* **59**, 1090–1 (1937)—C.A. **31**, 5322.
483. L. Wessely and Foedor Lynen, *Federation Proc.*, **12**, 685 (1953).
484. H. E. Westlake, Jr., and Gregg Dougherty, *J. Am. Chem. Soc.*, **63**, 658–9 (1941)—C.A. **35**, 2855.
485. J. Wexler, Harry Eagle, H. J. Tatum, H. J. Magnuson, and E. B. Watson, *J. Clin. Invest.*, **25**, 467–73 (1946)—C.A. **41**, 3539.
486. V. P. Whittaker, *Biochem. J.*, **41**, 52 (1947)—C.A. **41**, 4578.
487. Theodor Wieland and Ekkehart Bokelmann, *Ann.*, **576**, 20–34 (1952)—C.A. **47**, 2698.
488. H. Will and W. Körner, *Ann.*, **125**, 257 (1863).
489. H. Will and A. Laubenheimer, *Ann.*, **199**, 150–64 (1879).
490. A. H. Williams and F. N. Woodward, *J. Chem. Soc.*, **1948**, 38–42—C.A. **42**, 4930.
491. J. R. Wood, *Chem. Corps J.*, **2**, No. 3, 6–12, 51 (1948)—C.A. **42**, 2369.
492. F. N. Woodward, (a) *J. Chem. Soc.*, **1948**, 1892–4; (b) *Analyst*, **74**, 179–82 (1949); (c) *Brit. pat.* 585,655 (1947)—C.A. **43**, 2935, 6114; **45**, 9076.

493. Fritz Wrede, (a) Ber., 52, 1756-61 (1919); Z. physiol. Chem., 119, 46-59 (1922); (b) Deut. med. Wochschr., 50, 1611-2 (1925); *ibid.*, 51, 148-9 (1925); (c) Ger. pat. 563,875 (1927)—C.A. 14, 1546; 16, 3637; 20, 2148; 27, 1094.
494. Fritz Wrede, Emil Banik, and Otto Brauss, Z. physiol. Chem., 126, 210-8 (1923)—C.A. 17, 3030.
495. Fritz Wrede and Otto Hettche, Z. physiol. Chem., 172, 169-78 (1927)—C.A. 22, 581.
496. Leslie Young, Science, 103, 439-40 (1946)—C.A. 40, 3543.
497. Yu. K. Yur'ev, Kh. M. Minachev, and K. A. Samurskaya, J. Gen. Chem. (USSR), 9, 1710-6 (1939)—C.A. 34, 3731.
498. T. Zincke and R. Dereser, Ber., 51, 352-60 (1918)—C.A. 12, 2559.
499. T. Zincke and C. Ebel, Ber. 47, 923-33, 1100-8 (1914)—C.A. 8, 1781, 2164.
500. T. Zincke and P. Jörg, Ber., 42, 3362-74 (1909)—C.A. 4, 169.
501. T. Zincke and J. Müller, Ber., 46, 775-86 (1913)—C.A. 7, 1720.
502. T. Zincke and J. Ruppertsberg, Ber., 48, 120-9 (1915)—C.A. 9, 1058.
503. T. Zincke and F. Schütz, Ber., 45, 471-83 (1912)—C.A. 6, 1295.

CHAPTER 5.

Mercapto-Acids

A mercapto-acid is one in which the $-SH$ is substituted for a hydrogen atom of the alkyl. Thus $HSCH_2COOH$ is mercapto-acetic acid. However, this acid is commonly called thioglycolic acid and $CH_3CH(SH)COOH$ is thiolactic, the prefix "thio" showing that the $-SH$ group takes the place of $-OH$.

Thioglycolic Acid

Thioglycolic acid is found in the blood.³⁶² Thioglycolic and thiolactic acids are among the decomposition products of proteins³⁶⁶ and thiolactic can be obtained by the hydrolysis of wool.⁴⁹⁵

Thioglycolic acid, $HSCH_2COOH$, was prepared by Carius from chloracetic acid and potassium hydrosulfide.^{104a} Its potassium, barium, lead, and silver salts were studied. It was obtained also as a by-product in the preparation of thiodiglycolic acid.⁵²⁸ The ethyl ester was prepared from ethyl chloracetate.⁶³⁶ Claus made the acid from thiourea.¹²⁴ This has been considered recently.¹⁵¹

The solution of potassium thioglycolate resulting from the reaction of chloracetic acid with potassium hydrosulfide may be concentrated and a large amount of alcohol added to get rid of other salts. The alcohol is evaporated and the thioglycolic acid set free with sulfuric acid and taken up in ether.^{344a} Or, the acid may be isolated as the sparingly soluble barium salt.³⁴⁵ A high yield is said to be obtained from mixing a 20% solution of chlora-

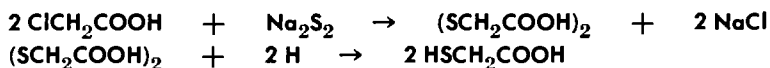
436

cetic acid with double the calculated amount of a 15% potassium hydrosulfide solution: ³⁴⁵

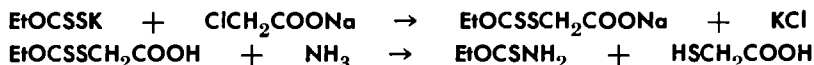


The displaced hydrogen sulfide keeps down the potassium sulfide concentration. A 99% yield is claimed from freshly prepared sodium hydrosulfide.⁵²⁶ The concentrations of the reactants and the reaction conditions affect the yield greatly.

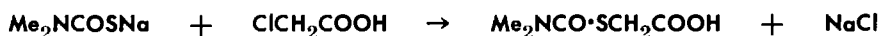
More or less of the sulfide acid, $\text{S}(\text{CH}_2\text{COOH})_2$, is obtained along with the thioglycolic by this reaction. To avoid this, it has been proposed to prepare the disulfide acid and reduce it: ^{231, 232, 299, 331, 368c, 369a}



As sodium disulfide may contain some of the monosulfide, sodium tri- or tetra-sulfide may be used. The reduction may be effected by zinc and acid,^{231, 232, 299} or electrolytically.^{368c, 369a} Thioglycolic acid may be made from a xanthate: ^{66a, 66b, 66c, 186, 231, 295a, 295c}



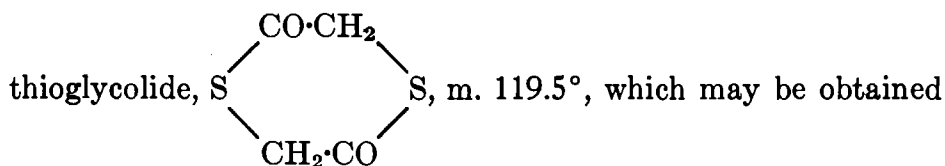
A thiocarbamate, from carbon oxysulfide and dimethylamine, may be caused to react with chloracetic acid: ^{332a}



Sodium thiosulfate has been used.^{105, 398} Detailed directions for the preparation from this material are given in a recent patent. A yield of 93% is claimed.^{138, 249.5} Thioglycolic acid can be obtained from thiocyanacetic acid.^{281, 306} Thiohydantoin heated with barium hydroxide gives the barium salt of thioglycolic acid.^{11a, 125} Similarly, nitrosothioglycolic acid is obtained from nitrosothiohydantoin³⁹⁶ and the isonitroso from isonitroso-pseudothiohydantoin.¹⁷² Diphenylthiohydantoin with alcoholic potash,³⁸⁵ or phenyl mustard oil glycolid and barium hydroxide, give thioglycolic acid. It has been obtained by a series of reactions starting from sulfoacetic acid.⁵³⁹ A mixed anhydride, $\text{HSCH}_2\text{CO} \cdot \text{O} \cdot \text{COCH}(\text{SH})_2$, results from the treatment of glyoxalic acid with hydrogen sulfide in the presence of silver oxide.^{75a}

The pure acid may be obtained by vacuum distillation. At room temperature, self-condensation goes on slowly. A 98% acid

may lose 3 to 4% in a month. The rate of reaction depends on the amount of water present.⁴²⁵ It is customary to add 15% of water to retard the condensation. On long standing, the acid is converted into water and an insoluble polymer.⁴⁶⁷ When an indifferent gas is passed for several days through the acid kept at 120°, water is eliminated and a viscous liquid remains. Along with polymers, this contains a large proportion of the dimeric



by vacuum distillation. This is hydrolyzed rapidly by alkali to the acid, $\text{HSCH}_2\text{COSCH}_2\text{COOH}$, which is hydrolyzed slowly to thioglycolic acid.^{520b}

The corresponding seleno-acid, $\text{HSeCH}_2\text{COOH}$, has been obtained from the hydrolysis of the selenocyano-acid, $\text{HOOCCH}_2\text{-SeCN}$.⁴⁰

Thioglycolid, $(\cdot\text{SCH}_2\text{CO}\cdot)_n$ has been described.³⁴⁵ The photochemical properties of thioglycolic acid have been studied.³⁴⁹

The salts of thioglycolic acid are of interest on account of their variety and of their therapeutic applications. As an acid, it forms salts and as a mercaptan, it forms mercaptides; a metal may be at either end or at both ends and different metals may be at the two ends. By use of these mixed salts, separation of some of the heavy metals may be effected.⁴⁰⁵ Many of its salts are known.⁴⁵³

The first salts made were those of potassium, barium, lead and silver,^{104a} but, as pointed out by Klason, the thioglycolic acid which Carius had was largely the sulfide-acid $\text{S}(\text{CH}_2\text{COOH})_2$.^{344a} These were followed by $\text{Hg}(\text{SCH}_2\text{COOH})_2$, $\text{Hg}(\text{SCH}_2\text{COO})_2\text{Ba}$, $\text{Hg}(\text{SCH}_2\text{COO})_2\text{Hg}$, $\text{Hg}_3(\text{SCH}_2\text{COO})_6\text{Al}_2$, $\text{Hg}(\text{SCH}_2\text{COO})_2\text{Mn}$, $\text{Hg}(\text{SCH}_2\text{COO})_2\text{Pb}$, $\text{Cd}(\text{SCH}_2\text{COO})_2\text{Cd}$, $\text{AgSCH}_2\text{COOAg}$, $\text{Pb}(\text{SCH}_2\text{COO})_2\text{Pb}$, $-\text{SCH}_2\text{COOBa} \cdot 3\text{H}_2\text{O}$ (0.85 g. dissolves in 100 g. of water at 17°), $\text{As}(\text{SCH}_2\text{COOH})_3$, $\text{Pt}(\text{SCH}_2\text{COOH})_2$,³⁴⁵ and the much used antimony salt, $\text{HOOC-CH}_2\text{SSbSCH}_2\text{COO-}$,^{345, 477} $\text{NaOOCCH}_2\text{SSbSCH}_2\text{COO-H}_2\text{O}$, $\text{Ba}(\text{OOCCH}_2\text{SSbSCH}_2\text{COO-})_2 \cdot 2\text{H}_2\text{O}$,⁴⁶² $\text{MgSCH}_2\text{COO-}$, $\text{MnSCH}_2\text{COO-}$, and $\text{As}(\text{SCH}_2\text{COONa})_3$.⁴⁷⁸ Stannic chloride and thioglycolic acid give the half-way salt, $\text{Cl}_2\text{Sn}(\text{SCH}_2\text{COOH})_2$,

which hydrolyzes to $(\text{HO})_2\text{Sn}(\text{SCH}_2\text{COOH})_2$.^{296a} Such products have been recommended as additions to hydrocarbon lubricants.¹⁹⁹ The physiological effects of a number of salts were studied by Myers:⁴²⁷ $\text{Bi}(\text{SCH}_2\text{COOH})_3$, $\text{CuSCH}_2\text{COOH}$, $\text{RbSCH}_2\text{COONa} \cdot 2\text{H}_2\text{O}$, $\text{AgSCH}_2\text{COONa}$, $\text{AuSCH}_2\text{COONa} \cdot \text{H}_2\text{O}$, $\text{BeSCH}_2\text{COONa}$, $\text{Cd}(\text{SCH}_2\text{COONa})_2 \cdot 4\text{H}_2\text{O}$, $\text{Hg}(\text{SCH}_2\text{COOH})_2$, $\text{Tl}(\text{SCH}_2\text{COOH})_3$, $\text{Ce}(\text{SCH}_2\text{COONa})_3$, $\text{Pb}(\text{SCH}_2\text{COONa})_2 \cdot 2\text{H}_2\text{O}$, $\text{V}_2(\text{SCH}_2\text{COONa})_3 \cdot 2\text{H}_2\text{O}$, $\text{As}(\text{SCH}_2\text{COONa})_3 \cdot \text{H}_2\text{O}$, $\text{Sb}(\text{SCH}_2\text{COO})_2\text{Na}$, $\text{Mo}(\text{SCH}_2\text{COONa})_4$, $\text{W}(\text{SCH}_2\text{COONa})_6 \cdot 2\text{H}_2\text{O}$, $\text{UO}_2(\text{SCH}_2\text{COONa})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{SCH}_2\text{COONa})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{SCH}_2\text{COONa})_2 \cdot 6\text{H}_2\text{O}$, $\text{Pt}(\text{SCH}_2\text{COOH})_4$, and $\text{Zn}(\text{SCH}_2\text{COONa})_2 \cdot \text{H}_2\text{O}$. The reaction of thioglycolic acid with mercuric chloride seems to go in two stages:^{538c}



Polarographic studies have been made of the mercury salt.^{378.5a, 562.5} Thioglycolic acid reduces stannic ions to stannous.⁵³⁸

A number of alkyl-mercury compounds, $\text{RHgSCH}_2\text{COOH}$, have been prepared.⁴⁸⁵ The methyl melts at 87° , the ethyl at 79° , the propyl at 73° and the butyl at 68° .^{339b}

Silver sodium thioglycolate, which is said to be valuable in treating diseases due to gonococci, can be prepared in several ways.^{113, 265} The antimony-calcium salt, $\text{Sb}_2(\text{SCH}_2\text{COO})_6\text{Ca}_3 \cdot 3\text{H}_2\text{O}$, is said to be a spirilloicide.^{264a} The antimony sodium salt is active against trypanosomes.¹¹⁵ Salts containing pentavalent antimony and an alkali metal are also spirilloicides.^{264b} From the antimony compound, $\text{HOOCCH}_2\text{SSbSCH}_2\text{COO}-$, m. 202° , the sodium, ammonium, zinc, and magnesium salts have been prepared.⁶¹⁴ The sodium antimony salt has been used for schistosomiasis.¹¹² Its toxicity and pharmacological action have been studied.⁴⁴⁵ The corresponding bismuth sodium thioglycolate has been investigated.³⁷¹ It is said to have antisiphilitic activity¹⁷⁹ and to check therapeutic malaria temporarily.⁵²⁹ Its intramuscular absorption has been studied.⁵⁵³ It is not accumulated in the kidney of a rabbit sufficiently to show an x-ray picture.³⁵⁷ The bismuth calcium salt is said to be useful.¹¹⁹ The lead sodium salt, $\text{Pb}(\text{SCH}_2\text{COONa})_2$, has low toxicity.^{394b} Arsenic and antimony derivatives are components of certain medicinal preparations.²³⁰

Calcium, strontium, and magnesium aurothioglycolates are

suitable for use by injection.¹⁵⁵ The gold calcium salt is effective against arthritis in mice.^{488, 489a} It inhibits cleavage of acetylcholine by cholinesterase.²³⁹ The preparation of the gold strontium salt has been described.^{160b} Auomercapto acids are prepared from auric salts in the presence of sulfur dioxide⁵¹⁰ or of neutral sulfites.⁵⁰⁹

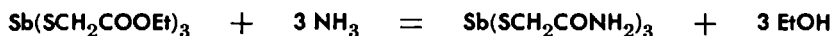
Two series of salts which are apparently derivatives of pentavalent antimony have been obtained. The acid in one of these is supposed to be $\text{Sb}(\text{SCH}_2\text{COOH})_5$.^{316b} Complex ferrous salts are known.^{378.3, 378.5b}

Uranyl thioglycolate is yellow-green, doubly refractive, and soluble in 30 parts of water.³⁵⁵ The reaction of thioglycolic acid with cupric ions is characteristic. The product appears to be the cuprous mercaptide cupric salt, $\text{CuSCH}_2\text{COOCuOH} \cdot 5\text{H}_2\text{O}$.^{173b} The calcium salt, $\text{CaSCH}_2\text{COO} \cdot 3\text{H}_2\text{O}$, loses water above 95° . Its solubility in 100 g. of water is 7 g. at 25° and 27 g. at 95° .³⁰⁶

Salts of thioglycolic acid are stabilized against oxidation by aliphatic diamines.^{340b} The pyridine salt of antimony ethylene mercaptide thioglycolic acid, $(\cdot\text{CH}_2\text{S})_2\text{SbSCH}_2\text{COOH}$, melts at 101° .¹²⁰ The absorption spectra of solutions of cobalt complexes of thioglycolic acid have been compared with those of cysteine.^{525a}

The ethyl ester of thioglycolic acid, $\text{HSCH}_2\text{COOEt}$, is a true mercaptan and forms mercaptides, $\text{KSCH}_2\text{COOEt}$, $\text{Pb}(\text{SCH}_2\text{COOEt})_2$, $\text{AgSCH}_2\text{COOEt}$, $\text{ClHgSCH}_2\text{COOEt}$, $\text{Hg}(\text{SCH}_2\text{COOEt})_2$, m. 56.5° ,⁶³⁶ and $\text{Ni}(\text{SCH}_2\text{COOEt})_2$, m. 101° .¹⁷⁰ Antimony trioxide may be dissolved in the ester to form $\text{Sb}(\text{SCH}_2\text{COOEt})_3$, an oil which has given favorable results as a trypanocide.⁴⁸⁴ Other compounds, $\text{Bi}(\text{SCH}_2\text{COOEt})_3$ and $\text{AgSCH}_2\text{COOEt}$, m. 77° , can be made similarly.⁴⁸² The gold, silver, and bismuth compounds of various esters have been claimed as therapeutic agents.⁵²⁴ The absorption and toxicity of the bismuth derivative of the ester have been studied.³⁷¹ Triphenyl-bismuth and thioglycolic acid give a yellow powder.²⁵² The dipole moment of the octyl ester has been studied.^{168.5}

The antimony derivative of the ester can be converted into the amide:⁴⁸⁴



The antimony derivative of the amide melts at 139° ²⁶⁹ and the bismuth³⁷¹ at 144.5° .²⁶⁹ These derivatives can be made from

thioglycolic amide prepared from chloracetamide.⁵ Antimony thioglycolamide is effective in the treatment of bilharziasis and trypanosomiasis.⁵³² Gold mercaptides of the N-alkyl amides have been prepared.^{620b} The gold derivative of thioglycolanilid gives an intense purple color with selenium oxychloride.^{620a} The gold derivative of the *o*-hydroxyanilide is relatively nontoxic.³⁸² The copper, mercury, silver, and zinc salts of substituted anilides have been claimed as therapeutic agents.^{620.5}

The acid, MeEtAsSCH₂COOH, melts at 82°. ⁶²⁷ An arylar-senious oxide reacts with thioglycolic acid ^{29c, 193, 256, 266, 446b} or its ester: ^{401, 446b, 551}



The same compound can be made from phenyldichlorarsine: ^{339a}



An antimony derivative can be made similarly:



The compound, *p*-AcNHC₆H₄As(SCH₂COOH)₂, melts at 110°. ¹²⁸ Aryl arsonic acids react with thioglycolic acid, its amide, or its esters to form thioarsenites, ArAs(SCH₂COOH)₂, ArAs-(SCH₂CONH₂)₂, or ArAs(SCH₂COOR)₂, which have definite melting points and may be used for the identification of these acids. ^{29a} Aryl arsonic acid derivatives, free acids, ArAsO-(SCH₂COOH)₂, amides, ArAsO(SCH₂CONH₂)₂, and esters, ArAsO(SCH₂COOR)₂, have been prepared. ^{29b, 30} Aryl arsonic acids may react with four, as well as with two, molecules of thioglycolic acid giving compounds of the type ArAs-(SCH₂COOH)₄. ^{446a} The diphenylarsenic derivative, Ph₂AsSCH₂COOH, is from the diphenylarsenious oxide, (Ph₂As)₂O. ⁵⁷⁰

The Walden inversion in the formation of derivatives of thioglycolic acid has been investigated. ³⁸¹

Thioglycolic acid is a true mercaptan. The reactions of its salts with chloroacetic, bromoacetic, and iodoacetic acids have been studied extensively. ^{194, 282a, 284} With ethylene bromide and with trimethylene bromide the acids, (·CH₂SCH₂COOH)₂ ⁴⁷⁰ and CH₂(CH₂SCH₂COOH)₂, are formed. ⁴⁸¹ Sodium thioglycolate reacts with acetobromoglucose ³³⁴ and with phenacyl bromide. ^{294b} Thioglycolic acid reacts quantitatively with chloroacetic acid in the presence of alkali. Using a known amount and titrating the

excess with iodine serve to determine the chlorine.⁶⁰⁴ Compounds of the type $\text{RCONHCH}_2\text{SCH}_2\text{COOH}$ can be prepared from N-chloromethyl amides.⁵⁵⁰

Thioglycolic acid is oxidised by iodine^{66a, 344b} or ferric chloride.^{253, 344b, 641} Its oxidation by various salts has been studied.^{39, 535, 626a}

The absorption of gaseous oxygen by a solution of this acid goes on slowly but steadily for several days. The rate is tripled by the presence of 0.000,001 mole per liter of a manganese salt.^{592a} The autooxidation causes weak luminescence which is stronger in the presence of the copper ion.^{303a} When oxygen is passed through a solution of thioglycolic acid, hydrogen peroxide is formed.⁵⁰³

In the presence of barium or sodium hydroxide, the oxidation is rapid, the speed depending on the concentration of the alkali. It does not stop at the disulfide. Oxalic acid is the chief product. Copper is an active catalyst.^{71, 519c} Iron and manganese ions are also.³⁷⁷ The rate of oxidation is not proportional to the concentration of the catalyst or to that of the thioglycolic acid.¹⁸⁹ The oxidation of the anilide is catalyzed by traces of selenium.⁶²

The oxidation-reduction potentials of thioglycolic and of thiolactic acids and the equilibrium:



have been studied.^{85a, 209, 249, 369b, 487a} Recent determinations correct old values.^{223.5} With L-cystine, thioglycolic acid comes to a reversible equilibrium at the half-way point. The free energy change is practically zero.⁶³ This applies not only to free cystine but also to the cystine units which link together protein chains.⁷⁴ The keratin in wool is reduced by it.^{190, 448, 519f} Its salts are used extensively in hair-waving preparations^{4, 337.5, 376, 418, 457.5, 517.5} and in depilatories.^{76, 196, 197, 210, 212, 545, 599} There have been investigations of possible toxicity.^{74.5, 102, 146, 256.5, 395, 423.5, 553.5} The triethanolamine salts of thioglycolic, thiolactic, and thioglyceric acids have been suggested for such uses.¹⁴⁷ Thiolactic acid is coming into larger use. It is said to be less toxic.⁴¹⁸ The theory of their use in hair waving is that the cystine linkages in the keratin of the hair are loosened by reduction to cysteine. After the hair is curled new cystine

linkages are formed by oxidation and the hair retains its set. Thioglycolic acid reduces glyotoxin to its sulfhydryl form¹⁷⁷ and pyruvic acid to lactic.³³ A review has been written on the scope and content of patents relating to the use of mercaptans in hair waving.^{561,5}

In the body of a rabbit, thioglycolic acid is readily oxidised, much of the sulfur appearing as the sulfate ion.²⁸⁸ It decolorizes methylene blue¹⁶⁵ and reduces nitrous acid to nitrogen.³⁹⁰ This may be analogous to what goes on in living tissues.⁵⁶²

In the presence of thioglycolic acid, linoleic acid takes up one atom of oxygen. As tests for carbonyl and hydroxyl groups are negative, the product must be of the ethylene oxide type. Formic acid is oxidised by air to carbon dioxide in the presence of thioglycolic acid and of iron, but not when only one of these is present. It has been suggested that mercaptan peroxides are concerned in respiration.⁵⁶⁸ The fact that thioglycolic acid is active only when a heavy-metal ion is present may indicate that the active agent is a mercaptide peroxide. It has been shown that lead mercaptides do form peroxides.⁴⁴² Thioglycolate salves have been suggested for skin disorders.^{354,5}

A nitrile, thioglycolic acid, and hydrogen chloride unite:



These iminoester salts can serve to identify nitriles. Their decomposition points are only fairly distinctive, but they can be titrated as dibasic acids. If the boiling point of the nitrile has been determined, its identification is satisfactory.^{130, 154} Iminoesters will be discussed again in the chapter on thioacids.

Thioglycolic acid adds to potassium cyanate:



Thioglycolic acid adds itself to many unsaturated compounds. The addition is so complete that it may be used for determining unsaturation in the same manner as iodine. Weighed amounts of an oil and the acid are mixed. After standing for a time, the excess of the reagent is back titrated with iodine. In a number of analyses the values found were one to three units higher than with iodine.¹⁸ There is no possibility of substitution as there is with iodine or bromine. The rates of addition of

thioglycolic acid to various olefins under different conditions have been measured in order to lay a basis for its use in the analysis of mixtures.³⁰⁴ This method seems worthy of further study. The fact that addition takes place with some unsaturates and not with others gives it a diagnostic value, particularly when used in conjunction with iodine. As thioglycolic acid is unstable, frequent standardization is required. There is the possibility that the addition may be influenced by traces of metals or by peroxides which may be present.

Thioglycolic acid has been added to an unsaturated higher alcohol under controlled conditions.^{162, 308} It reacts quickly with styrene, in the presence of ascaridole, to form β -phenylethylthioglycolic acid, $\text{PhCH}_2\text{CH}_2\text{SCH}_2\text{COOH}$. In the presence of hydroquinone and in the absence of air there is no addition.³⁴² The presence of a peroxide seems to be necessary, but the amount required is so small that the traces of peroxides, which are almost always present in organic compounds, are ample. When thioglycolic acid is poured into an equivalent amount of undecylenic acid, the mixture gets hot and, on cooling, sets to a solid mass of the addition product.⁴⁶⁷ Pale-crepe rubber, after being in contact with thioglycolic acid for 16 months, dissolved largely in aqueous sodium hydroxide. The addition of acid precipitated a substance in which the $\text{C}_5\text{H}_8:\text{HSCH}_2\text{COOH}$ was 1:0.953.^{293c, 328} In another experiment, this ratio was 1:0.67.³³³ Butadiene copolymers are made more resistant to hydrocarbon solvents by the partial saturation of the double bonds with thioglycolic acid.⁵³¹ Thioglycolic acid and phenyl vinyl sulfone give the acid, $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{COOH}$, m. 84° .²¹⁴

Thioglycolic acid reacts readily with aldehydes and ketones to form mercaptals, $\text{RCH}(\text{SCH}_2\text{COOH})_2$, and mercaptoles, $\text{RR}'\text{C}(\text{SCH}_2\text{COOH})_2$.^{77, 294d, 296b, 299, 537, 561} The formation of these may serve to identify carbonyl compounds.^{475.5} Its esters react similarly.⁴²⁶ These products will be treated in the chapter on mercaptals and mercaptoles. The compound with glucose is particularly stable.^{296c} The anilide of thioglycolic acid forms hemiacetals with aldehydes.^{525e} The acid forms addition compounds with hydroascorbic acid,¹⁶⁸ with methylglyoxal,^{525d} and with quinone and naphthaquinone.²⁰⁶

Thioglycolic acid reacts with formic acid like a simple mer-

captan to form the trithio-orthoformate, $\text{HC}(\text{SCH}_2\text{COOH})_3$, m. 173° .^{293a, 299, 307} The xanthate, $\text{KS}\cdot\text{CS}\cdot\text{SCH}_2\text{COOK}$, is formed with carbon disulfide and alkali.^{295b} Thioglycolic acid unites with cyanamide to form the isothiuronium complex, $\text{H}_2\text{N}(\text{HN}:)-\text{CSCH}_2\text{COOH}$, which goes into 2-imino-4-thiazolidone with the loss of a molecule of water.^{11b} With potassium thiocyanate the product is 2-thio-4-thiazolidone.²²⁷

Thioglycolic acid has been used in the study of cellulose^{93, 300} and of lignin.^{84, 224, 293c, 295c, 297, 474, 514, 515} With lignin it forms a product represented by the formula, $\text{C}_{40}\text{H}_{40}\text{O}_{12}\cdot n\text{HSCH}_2\text{COOH}$, in which n varies between 3 and 4.^{54, 296d} Some of the thioglycolic acid may be split off by methylation.⁹ The 5-pseudocumylacetone isolated from crude wood spirit and the synthetic compound react with thioglycolic acid to form 5-pseudocumylmercaptolacetic acid, m. $146-8^\circ$.^{293b} These investigations have been summarized by Holmberg.^{296e}

Acetylthioglycolic acid, $\text{MeCOSCH}_2\text{COOH}$, may be made from the acid and acetyl chloride or from thioacetic acid and chloroacetic acid.^{47, 621} Its acid chloride, $\text{MeCOSCH}_2\text{COCl}$, reacts with the sodium derivative of cyanacetic ester to give ethyl acetylthioglycolylcyanacetate, $\text{MeCOSCH}_2\text{COCH}(\text{CN})\text{-COOEt}$, m. 71° .⁴⁷ The benzoate, $\text{PhCOSCH}_2\text{COOH}$, can be made from the acid and benzoyl chloride or from sodium thio-benzoate and chloroacetic acid.^{294e} The trichloroacetyl derivative, $\text{Cl}_3\text{CCOSCH}_2\text{COOEt}$, has been used in a high-pressure lubricant.^{275.5}

Ethyl thioglycolate is obtained in 89% yield by refluxing a mixture of the acid, ethanol, sulfuric acid, and benzene under a Soxhlet containing magnesium sulfate.²⁶ The glycerol ester has been obtained by the aid of xylene to entrain the water.⁴⁵⁸ Polyvinyl alcohol can be esterified and the ester oxidised to the disulfide.⁴²⁰ The fresh ester is soluble in water, but becomes insoluble, due to the cross linking by $-\text{SS}-$ from air oxidation.³⁶¹ The reaction product of linseed oil with glycerol is esterified with thioglycolic acid.⁴²⁰ Esters, HSCH_2COOR , in which the alkyl contains two to eight carbon atoms are claimed as constituents of high-pressure lubricants.⁶²⁸

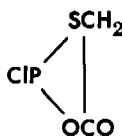
The amide is made by the action of dry ammonia on an ester.^{345, 552} It was a by-product in the preparation of the sulfide, $\text{S}(\text{CH}_2\text{CONH}_2)_2$.⁵²⁸ The anilide has been prepared by

refluxing a mixture of the acid, aniline,^{283a} and benzene with water take-off.⁶⁰¹ Substituted anilides, which are used in color photography, are made from the acid chloride and substituted anilines.⁶²¹

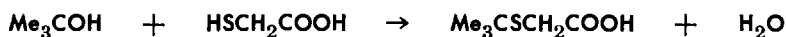
Alkyl sulfides, $\text{RSCH}_2\text{CONHC}_7\text{H}_7$, have been made from the ortho, meta and para toluides, $\text{HSCH}_2\text{CONHC}_7\text{H}_7$.^{39a} Derivatives of this sort have been recommended for the identification of alkyl halides. They may be oxidised to sulfoxides by hydrogen peroxide.^{283a} In case the sulfide is an oil, the sulfoxide melting point may serve for identification. If both are solids, two melting points are available. These are sulfide-acid derivatives and the melting points are to be found in the pertinent chapter. The thionitrite, $\text{PhNHCOCH}_2\text{SNO}$, m. 160° , and a thiocarbamate, $\text{PhMeNCOCH}_2\text{SCONH}_2$, have been prepared.⁴⁷¹ A sulfonamide derivative, $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHCOCH}_2\text{SH}$, has been patented.^{119.5}

Thioglycolic acid is desulfurized by Raney nickel to acetic acid.⁷⁹

With phosphorus trichloride, a cyclic compound is obtained: ¹⁸



Thioglycolic acid reacts in a curious way with tertiary alcohols:



Many derivatives have been made from this sulfide acid.^{283b} Benzyl and α -phenylethyl alcohols react similarly. The products are the sulfide acids, $\text{PhCH}_2\text{SCH}_2\text{COOH}$ ^{295d} and $\text{PhCHMeSCH}_2\text{COOH}$.^{294c} From benzoin, the compound, $\text{PhCOCHPhSCH}_2\text{COOH}$, is obtained ⁴¹ and also the stilbene, $\text{PhC}(\text{SCH}_2\text{COOH})\text{:C}(\text{SCH}_2\text{COOH})\text{Ph}$.⁵⁸⁵

Lactic acid is destroyed by oxygen in the presence of thioglycolic acid.³⁹⁷ The imidazole ring of histidine is broken by oxygen and this acid.^{302, 303b} It influences the oxidation of several compounds by hydrogen peroxide in the presence of iron.^{303b, 626b} The catalysis of oxidation may be connected with the formation of complexes of thioglycolic acid with heavy metals, such

as $\text{Co}(\text{SCH}_2\text{COO})_2\text{KH}$, $\text{Co}_2(\text{SCH}_2\text{COO})_4\text{KH}_3$, $\text{Co}_2(\text{SCH}_2\text{COO})_4\text{-BaH}_2$, $\text{Co}(\text{SCH}_2\text{COOH})_2$.^{412, 535} The catalytic effect of copper on the oxidation of thioglycolic acid is stopped by hydrocyanic acid which forms a complex with the copper.^{410b} Thioglycolic acid protects against cyanide⁶¹³ and is antagonistic to carbon tetrachloride⁹¹ and thiourea.¹⁶¹ It diminishes the damage to the liver of an animal on a fat diet. Thiomalic and thiolactic acids do not have this effect.²⁵⁷ The addition of sodium thioglycolate to an arsenical inhibits completely its effect on the virulence of trypanosomes.⁴⁶⁹ It neutralizes the bacteriostatic effect of mercuric chloride⁴³⁷ and counteracts the diuretic action of organic mercurials.²⁶⁸

Aerobic and anaerobic oxidations of sulfhydryl compounds are catalyzed by dithioglycolic acid.^{272b} A peculiar kind of oxidation in washed acetone yeast is brought about by thioglycolic acid.^{410a} Iodoform is destroyed in the presence of it, or of thiolactic acid.^{592a} Thioglycolic acid, however, is recommended as an oxidation inhibitor for organic compounds in general and its sodium salt for amines.^{316a, 316c, 527} It is a stabilizer for solutions of quinine and quinoline derivatives⁵²⁷ and for polysulfone resins.³¹⁷ It inhibits the oxidation of leuco-methylene blue.^{519a} It is useful as a modifying agent in the emulsion polymerization of chloroprene^{176a} and or GRS.⁵⁴⁸ It inhibits the autooxidation of hydroquinone by tying up the quinone.³²⁰ Thioglycolic and β -mercaptopropionic acids desensitize photographic paper and emulsions.³⁴⁹

Methyl, ethyl, butyl, benzyl, phenyl, and naphthyl mercuric thioglycolic acids, $\text{RHgSCH}_2\text{COOH}$, inhibit the growth of tubercle bacillus at 1:500,000 dilution.¹²⁹ Cobra venom is detoxified by sodium thioglycolate or thiolactate.^{69, 70}

The gas gangrene group of anaerobes grows luxuriantly in a medium containing sodium thioglycolate.⁴⁶⁶ Such a medium is recommended for routine use in diagnostic bacteriology.⁴⁶⁸ Its presence seems to insure the proper oxidation-reduction equilibrium.⁸⁶ It promotes the growth of *Bacterium tularenses* less than cystine or cysteine.⁴⁶³

The swelling of potato starch is affected by thioglycolic acid.³³⁶ The rest period of dormant potato tubers is broken by it.⁴¹⁴ Cell proliferation of root hairs and of chick embryos is stimulated by thioglycolates.²⁶⁷ Plant growth is accelerated.^{386, 589}

Glucolysis by propionic bacteria is favored by thioglycolic and thiolactic acids.¹¹¹ Thioglycolic acid inactivates the lactogenic hormone fifty times as strongly as cysteine.^{218, 219b} Its influence on artificial peroxidase,⁴³⁸ on the process of regeneration of *Padarke obscura*,⁴¹⁹ and on the activity of papain have been investigated.⁶¹ The addition of thioglycolic acid to atoxyl increases its efficiency in killing trypanosomes,²²⁹ but the opposite effect on arsphenamine has been reported.¹⁸⁰

Thioglycolic acid is antagonistic to vitamin C,⁶¹⁸ urease,³¹⁹ insulin,⁶³³ streptomycin,¹⁶⁷ and gonadotropins.^{219a} It inhibits autolysis²³ and influences the respiration of baker's yeast.⁴⁸⁶ It may protect a virus against rapid aerobic inactivation.⁶⁴ The toxicity and repellancy of its esters to the larvae of flies has been investigated.³⁸⁸

Thioglycolic acid is useful in analytical chemistry as it forms colored complexes with metal ions.¹⁷¹ Iron can be detected and estimated by its use.^{335, 407} The color with ferric ions was first described as dark red,^{11a} but this color has been shown to be due to the presence of ferrous ions. Ferric ions give a blue color which is stable in acid solution but is discharged by alkali. Ferrous ions give a purple color in alkali. Both ferrous and ferric ions can be estimated in the same solution down to 1 part in 10,000,000.^{394a} In the absence of air the addition of potassium hydroxide to a solution containing thioglycolic acid and ferrous ions gives a yellow precipitate. On further addition of alkali, this dissolves, giving a deep orange-red solution containing $\text{Fe}(\text{SCH}_2\text{COOK})_2$.^{525b} In an ammoniacal solution the ferrous ion gives no color if air is excluded while the ferric ion gives a blue color due to the formation of $\text{Fe}(\text{SCH}_2\text{COONH}_4)_3$. This test is good for 0.13 gamma of iron or for 60 gamma of thioglycolic acid.^{173a} With isonitrosothioglycolic acid 3 gamma of iron can be detected, or 1 part in 7,000,000.¹⁷² Thioglycolic acid prevents the interference of iron in the estimation of aluminum.^{116, 310} Molybdenum can be determined photometrically by its aid.^{409, 473, 630.5} Palladium solutions give a yellow spot test down to 0.05 gamma of the metal.³⁵¹ Thioglycolic acid is recommended for the quantitative precipitation of metallic dryers from oils and varnishes.³⁸⁹

Thioglycolic acid gives a color reaction with a nitrite in acid solution^{484.5, 592b} and with a reagent containing basic fuchsin,

sulfuric acid, and formalin.⁵⁵⁴ Its presence can be proved by a combination of its reactions with phosphomolybdic acid and with mercuric chloride.^{536d} It can be titrated iodometrically.^{282b, 354, 369c} Methods for its potentiometric titration^{497, 498} and for its determination in the presence of sulfites^{92, 228a} have been given. With the aid of sodium 1,2-naphthoquinone-4-sulfonate, it can be estimated colorimetrically.^{228b} It can be determined by Folin's reagent, a phosphotungstic acid.^{306, 520a, 521, 536b, 536d} With the aid of sodium nitroprussate, it can be estimated spectrophotometrically.^{460.5} Thioglycolic acid catalyzes the decomposition of sodium azide by iodine.^{233b} By measuring the nitrogen evolved, it can be estimated down to 10 gamma.^{317.5}

Thioglycolic- β -naphthalide, $\text{HSCH}_2\text{CONHC}_{10}\text{H}_7$, sometimes called thionalid, is an excellent reagent for detecting metal ions. In 0.2 *N* acid, the limiting concentrations in gammas are: copper 0.1, silver 0.2, gold 0.4, mercury 0.06, tin 0.08, arsenic 0.01, antimony 0.02, bismuth 0.1, platinum 0.1 and palladium 0.1.^{55, 56, 57, 365, 549} It is recommended for the gravimetric estimation of osmium.⁷ The *p*-nitro⁹⁶ and the *p*-acetamino derivatives of the anilide are also recommended for the detection of heavy metal ions.⁹⁷ The 2-hydroxy-5-nitro derivative serves for the colorimetric estimation of cobalt.⁹⁶ The preparation of this has been described.^{96.5}

Thiolactic Acid

Thiolactic, α -mercaptopropionic, acid was first prepared by Schacht from α -chloropropionic acid and potassium hydrosulfide.⁵⁰² A 77% yield, free of sulfide acid, can be obtained by the xanthate method.^{66a, 66b} It has been prepared from thiosulfate.³⁹⁸ The reaction of thioacetic acid with α -bromopropionic acid gives the thioacetate which is readily hydrolyzed.²²¹ Thiolactic acid can be obtained by the reduction of the disulfide acid.^{369a} It was by the careful reduction of the resolved disulfide acid that the active thiolactic acids have been prepared.^{60, 391d}

α -Thiocyanopropionic acid, $\text{MeCH}(\text{SCN})\text{COOH}$, can be reduced to thiolactic.^{222b} When hydrogen sulfide is passed into a solution of pyruvic acid, or into a solution of its silver salt, one of the final products is thiolactic acid. The thioketone, MeCSCOOH , is probably formed and then reduced.^{75b, 567} This has been verified by comparison of the product with one from

α -chloropropionic acid.^{75c} The trisulfide acid, $\text{HOOCCHMeS}_3\text{-CHMeCOOH}$, can be desulfurized by alkali^{391c} or by sodium amalgam and later reduced.^{391d} The disulfide acid is not the only product of the desulfurization, but it can be isolated from the mixture.¹⁵³ Lactic acid has been distilled with phosphorus pentasulfide, but the results were indefinite.^{75a} The failure of this method of replacing OH by SH has been explained in Chapter 1.

Thiolactic acid is a minor product of the hydrolysis of proteins, though there is doubt that it is a primary one.^{233a, 360, 415b} Cystine hydrochloride heated in aqueous solution to 145° gives the disulfide acid, $(\text{SCHMeCOOH})_2$, which can be reduced.^{234, 415a} Thiolactic acid has been identified among the decomposition products of horn.⁵⁶⁷

Thiolactic acid mixes with water and is soluble in ether. It can be identified by its 3,5-dinitrobenzoyl⁴⁹⁹ or benzyl derivative which melts at 76.5° .²³⁴ It gives a transient blue color with ferric ions²¹⁷ and a blue-violet color with cupric ions.^{217, 415a} It gives a red color with nitrous acid.^{592b} On boiling, it blackens lead acetate.²¹⁷ Two forms, α - and β -, have been distinguished.³⁶⁰

The salts of thiolactic acid are similar to those of thioglycolic acid in that the metal may replace the hydrogen of either the mercaptan group or of the carboxyl and different metals may replace the two. The following salts are some of those that have been described. MeCH(SH)COOK , $(\text{MeCH(SH)COO})_2\text{-Ba}$, Hg(SCHMeCOOH)_2 , $\text{Hg(SCHMeCOO)}_2\text{Ba}$, AgSCHMeCOOH , Bi(SCHMeCOOH)_3 , CuSCHMeCOOH .^{391a} The antimony salt, $\text{HOOCCHMeSSbSCHMeCOO-}$, is made by dissolving antimony trioxide in the acid.⁶¹⁴ The uranyl salt is greenish, microcrystalline, and soluble in 40 parts of water.³⁵⁵ The gold salt has been prepared.^{508, 523} This salt is physiologically active.⁴⁵⁴ Thiolactic acid is useful in determining iron in biological materials.⁵⁹⁵ The ethyl ester gives the cuprous mercaptide, CuSCHMeCOOEt .^{391a}

Thiolactic acid is oxidised by iodine or ferric chloride to the disulfide acid.^{391a} The rate of oxidation by hydrogen peroxide depends on the pH of the solution and is catalyzed by iron.^{519d} The oxidation by gaseous oxygen is similar to that of thioglycolic acid but slower.^{71, 519c, 592c} Oxidation to the sulfo-acid, $\text{MeCH(SO}_3\text{H)COOH}$, does not change the direction of the rotation.^{379a, 379b} It is oxidised to the sulfo-acid by permanganate.²²

The oxidation-reduction equilibrium between thiolactic acid and the disulfide acid has been calculated from free energies and ionization constants.⁷⁸ The rate of oxidation has been studied.⁷¹

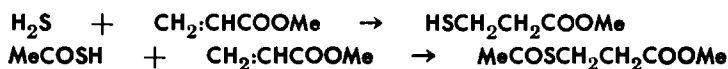
Thiolactic acid is oxidised readily in the body of a rabbit, half of the sulfur appearing in the urine as the sulfate ion. Below 0.25 g. per kilo it is nontoxic.²⁸⁸ Like thioglycolic acid, it produces a peculiar sort of oxidation in washed acetone yeast.^{410a} It inhibits the autooxidation of bisulfite.²⁴⁸

It is esterified by ketene to S-acetyl- α -mercaptopropionic acid, MeCH(SAc)COOH .⁴³¹ It is desulfurized to lactic acid by sulfurase.²³⁸ One molecule of thiolactic acid reacts exothermically with one of pyruvic to give a crystalline compound.²³⁵

Experiments similar to those with thioglycolic acid have been made with thiolactic acid in the treatment of wood.^{293d}

β -Mercaptopropionic Acid

β -Mercaptopropionic acid, $\text{HSCH}_2\text{CH}_2\text{COOH}$, frequently called β -thiolactic acid, can be made by standard methods, from β -halopropionic acid with potassium hydrosulfide,^{391a} or better with the xanthate,^{66b} or with thiourea.^{25, 117, 416, 417} It has been obtained by the hydrolysis of the thiourethane, $\text{H}_2\text{NCOSCH}_2\text{CH}_2\text{COOH}$,³⁶⁷ and of the thioacetate, $\text{MeCOSCH}_2\text{CH}_2\text{COOH}$, from the addition of thioacetic acid to acrylic acid.³⁰¹ Hydrogen sulfide,⁶⁰² or thioacetic acid,²²¹ may be added to methyl acrylate:



These can be hydrolyzed to the acid. A recent method is the reaction of β -propiolactone with a cold solution of sodium sulfide.^{255, 259}

The disulfide acid disproportionates when treated with a mercuric or silver salt:⁴⁵⁹



When the acid is heated on a water bath with dilute hydrochloric acid, condensation takes place. The self-ester, $\text{HSCH}_2\text{CH}_2\text{COSCH}_2\text{CH}_2\text{COOH}$, m. 46° , is one of the products.^{294f}

This acid is analogous to thioglycolic in being both a mercaptan and an acid and exhibiting the reactions of both. It forms mercaptides, such as $\text{Hg(SCH}_2\text{CH}_2\text{COOH)}_2$, salts such as $\text{HSCH}_2\text{CH}_2\text{COONa}$, and mercaptide salts in which the same or

different metals may be on the two ends. The arylarsenic mercaptides, p -MeCONHC₆H₄As(SCH₂CH₂COOH)₂, m. 147°, ¹²⁸ and p -Me₂NC₆H₄As(SCH₂CH₂COOH)₂, ^{339c} have been described. The gold mercaptide is known. ⁴¹⁶ The alkyl-mercury derivatives, RHgSCH₂CH₂COOH, are said to have value. ^{339b} The lead salt is considered to be cyclic. ³⁴⁶ The acid has been recommended for the absorptiometric determination of nickel. ^{375.5}

β-Mercaptopropionic acid is oxidised by ferric chloride or by iodine to the disulfide acid which melts at 155° and is useful for its identification. ^{391a, 415a} The photochemical properties have been studied. ³⁴⁹ The methyl ester, HSCH₂CH₂COOMe, and the silver mercaptide, AgSCH₂CH₂COOMe·AgNO₃·H₂O have been prepared. ¹⁷⁰

β-Mercaptopropionic acid has some effect as an antidote for hydrocyanic acid. ²⁷⁷ It increases the physiological activity of auroglutathionate. ²⁰⁵ It prevents rancidity in edible oils. ^{259.5} The free acid, its sodium salt, and its ethyl ester are catalysts for the condensation of phenol with ketones. ³²³

Mercaptobutyric Acids

Mercapto acids have been made from α-bromo-*i*-butyric acid and from the three bromo derivatives of *n*-butyric acid by the usual reactions. ^{39a, 66a, 189, 178, 301, 324, 368d, 391b, 392, 504, 511, 619} In addition, there are special methods for some of them.

α-Mercaptoisobutyric acid has been obtained by the alkaline hydrolysis of 3-ethyl-5-dimethylthiazolidone-4. ⁸³ It can be titrated with phenolphthalein, ^{368b} but not with iodine in acetic acid solution. It is oxidised regularly by iodine in alkaline solution. ^{519e} β-Mercaptoisobutyric acid is obtained by the saponification of the thioacetate, AcSCH₂CHMeCOOH, from the addition of thioacetic acid to methacrylic acid. ^{223, 368d, 369d} Its methyl ester, HSCH₂CHMeCOOMe, can be prepared by adding hydrogen sulfide to the methacrylic ester. ^{94, 95} The acid can be titrated with iodine. ^{369d}

The ethylmercury salt of α-mercaptobutyric acid, EtHgSCH-EtCOOH, is water soluble. ⁶¹⁵ The anilide is recommended for use in color photography. ⁶²¹ Its gold derivative has been prepared ^{160b} and its toxicity to rats determined. ^{160a}

β-Mercaptobutyric acid has been prepared by the addition of thioacetic acid to crotonic acid and hydrolysis of the thioace-

tate.³⁰¹ Its ester is formed by the addition of hydrogen sulfide to a crotonic ester.^{114,5} Its sodium salt is formed when sodium hydrosulfide and sodium crotonate are brought together.¹⁹⁵ The ethyl ester is obtained by hydrogenating acetoacetic ester in the presence of sulfur.^{203, 374}

γ -Chlorobutyronitrile reacts with potassium hydrosulfide to give the γ -thiolactone⁶¹⁹ which can be converted to the acid or obtained from the acid.³⁰¹ The same thiolactone is formed when butyrolactone is heated with hydrogen sulfide under pressure in the presence of a catalytic amount of sodium hydrosulfide. This works also with δ -valerolactone.^{19,5} γ -Mercaptobutyric acid has been prepared by the addition of thioacetic acid to the butenoic acid, $\text{CH}_2\text{:CHCH}_2\text{COOH}$, and saponification of the thioacetate.³⁰¹ Its toxicity to men has been determined.⁸¹ An ester of mercaptobutyric acid improves the drying rate and luster of lacquers.²⁰

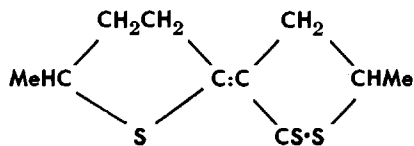
The rates of formation and of hydrolysis of thiolactones of mercaptobutyric acids and of higher acids of this class, including several dibasic acids, have been investigated. The delta lactones are hydrolyzed much more rapidly than the gamma.^{512c} A gamma or delta thiolactone is oxidised by halogens to the disulfide acid.²¹

Mercaptovaleric Acids

The mercaptovaleric acids may be prepared from the corresponding bromo-acids by either the sodium hydrosulfide or the thiourea method.^{178, 380, 391b} For several there are special methods.

β -Mercaptovaleric acid is obtained from the addition of thioacetic acid to propylideneacetic acid and the saponification of the thioacetate.^{512b, 563a} Hydrogen sulfide was added to β,β -dimethylacrylic acid to get β -mercaptoisovaleric acid.^{563a} Adding hydrogen sulfide to isopropylidenemalonic acid, $\text{Me}_2\text{C:C(COOH)}_2$, and decarboxylating yields the same result.²¹³

γ -Valerolactone can be converted to the thiolactone with phosphorus pentasulfide. This hydrolyzed to the acid, $\text{HSCHMeCH}_2\text{CH}_2\text{COOH}$.²³⁶ Some dithiolactone, $b_{15} 120^\circ$, is also formed. This condenses to



The same acid is obtained by the catalytic hydrogenation of levulinic acid in the presence of sulfur^{204a} and also through a hexathiazole from allylmalonic acid and thiourea.³²⁵ It is the end product when thioacetic acid is added to hydrosorbic acid and the thioacetate hydrolyzed.^{512a, 512b}

One synthesis of δ -mercaptovaleric acid starts with the addition of thioacetic acid to allylacetic acid^{512b} or to allylmalonic acid. This acid forms a thiolactone.^{512a} The same acid is obtained by hydrogenating δ -carbomethoxyvaleraldehyde in the presence of sulfur.^{204b} The same treatment transforms γ -ketovaleric acid into the thiolactone.²⁰³ α -Mercapto- β -hydroxy-*i*-valeric acid has been reported.^{398.5}

Higher Mercapto-Acids

The general synthetic methods that have been used for the lower mercapto-acids are available. The xanthate method is highly recommended.^{186, 205.5} A special method for the alpha acids is the hydrolysis of a pseudothiohydantoin, which can be made by condensing an α -bromoacid with thiourea⁴³⁴ or an ester of such an acid with carbon disulfide.⁵¹¹

γ -Mercaptocaproic acid and its thiolactone have been produced from hydrosorbic and thioacetic acids as starting materials.^{512a} ϵ -Mercaptocaproic acid has been prepared from the bromo-acid and potassium hydrosulfide.³¹⁸ γ -Mercapto-*i*-caproic acid has been obtained starting with unsymmetrical dimethylethylene sulfide.⁵⁴⁷

α -Mercapto- β -phenylpropionic acid has been obtained by hydrolysis of the xanthate⁶⁷ and β -mercapto- β -phenylpropionic acid by the reduction of β -mercapto- β -phenylacrylic acid.²⁰⁷

κ -Mercaptoundecylic acid has been prepared by the xanthate^{36, 127} and thiourea methods^{417, 464} and by reduction of the disulfide.^{127, 186} This is oxidised during recrystallization to the disulfide acid.¹²⁷ The arsenic derivative causes the rapid disappearance of trypanosomes from the blood stream.¹²⁷

α -Mercaptostearic acid has been prepared from the α -bromo acid and potassium hydrosulfide.¹⁸⁵

Mercaptoacids have been made from the addition products of thioacetic acid with unsaturated acids^{316d} and by hydrogenating sulfurized unsaturated acids or by hydrogenating unsatu-

rated acids in the presence of sulfur and a sulfactive catalyst.³⁷⁵ Gold derivatives of these acids, suitable for therapeutic use, can be made directly from the isothiuronium salts.^{416, 417}

A mercapto-acid may be added to unsaturates containing more than six carbon atoms to produce foaming agents.²⁸⁵ An injection of the bismuth salt of butyl mercaptolaurate causes rapid disappearance of lesions.¹³ Salts of auro-mercapto-cyclo-pentyl-acetic acid are claimed as therapeutic agents.⁴²⁴ Triamyl-ammonium mercapto-stearate and similar salts are said to impart film strength to lubricating oils.³⁸⁷

Ethyl β -chlorolactate reacts with potassium hydrosulfide to give ethyl β -thioglycerate, $\text{HSCH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOEt}$. Saponification of this yields the free acid, a syrup which cannot be distilled, 2,4-dinitrophenyl derivative, m. 168° . The acid is oxidised by air to the disulfide acid, a thick gum.³⁵⁰ The oxidation-reduction potential has been compared with that of thioglycolic acid.²⁰⁹

Ethyl β -chloroisocrotonate and potassium hydrosulfide give ethyl β -mercaptocrotonate, $\text{MeC}(\text{SH})\cdot\text{CHCOOEt}$.⁵⁰⁵ The iron, cuprous, and lead derivatives are characteristic. It can be methylated or acetylated. This is the thioenol form of thio-acetoacetic ester^{205,3} which is treated under thials and thiones. The methyl ester, $\text{MeC}(\text{SH})\cdot\text{CHCOOMe}$, is known.⁵⁰⁶

Mercaptoelaidic and mercaptoelaidic acids have been obtained from dithiocyanostearic and dithiocyanobehenic acids.⁴⁹⁴ α -Mercaptochaulmoogric,¹⁰⁰ 5-mercaptomethylfuroic,³⁴³ and 2-mercaptoethylamylbarbituric⁵⁴¹ acids have been prepared. The addition of hydrogen sulfide to croconic acid gives a gummy mass from which the lead salt, $\text{C}_5\text{H}_3\text{O}_4\text{SPb}$, has been isolated.³⁷⁸

Mercaptopyruvic acid, $\text{HSCH}_2\text{COCOOH}$, has been prepared from the haloacid and ammonium hydrosulfide.^{447a, 516, 517} Hydrogen sulfide is liberated when this is added to a fermenting sugar solution.²⁴² β -Mercapto- α -ketobutyric acid is prepared similarly^{447b} and is likewise decomposed by yeast.²⁴² Hydrolysis of the condensation products of aldehydes with 2,4-thiazolidinedione gives substituted α -thiopyruvic acids, such as furyl-, phenyl-, 3,4-dimethoxyphenyl- and 2-thienyl- α -thiopyruvic acids.³⁸⁴

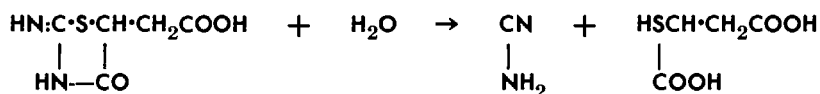
Dimercapto-Acids

α -Chloroacrylic acid takes up one molecule of thioacetic acid to form the thiolacetate, $\text{AcSCH}_2\text{CHClCOOH}$.⁴⁵¹ Its ester reacts with two molecules giving the dithiolester, $\text{AcSCH}_2\text{CH}(\text{SAc})\text{-COOMe}$.³⁷³ These thiolesters are readily saponified to the acid.^{198, 449} The acid, $\text{HSCH}_2\text{CH}(\text{SH})\text{COOH}$, prevents the inhibition of succinic oxidase by heavy metals.³⁴

β,β' -Dimercapto-*i*-butyric acid, $(\text{HSCH}_2)_2\text{CHCOOH}$, has been obtained by the reduction of the disulfide acid which has been isolated from asparagus. Desulfurization with Raney nickel gave *i*-butyric acid. The same *bis*-sulfide, $(\text{MeSCH}_2)_2\text{CHCOOH}$, was obtained by methylating the natural acid and by treating the diiodo-acid, $(\text{ICH}_2)_2\text{CHCOOH}$, with sodium methyl mercaptide.^{321, 322}

Dibasic Acids

Thiomalic, or mercaptosuccinic acid, $\text{HOOC}\cdot\text{CH}_2\text{CH}(\text{SH})\cdot\text{COOH}$, is obtained from bromosuccinic acid by potassium hydrosulfide^{104b} or through the xanthate.^{66a, 298, 479} By heating fumaric or maleic acid with thiourea and hydrolyzing the resulting thiohydantoin with barium hydroxide, the same acid is formed.^{11c, 11d} The thiohydantoin-acetic acid is split into cyanamide and thiomalic acid:⁵⁷¹



The addition of thioacetic acid to fumaric or to maleic acid gives the thioacetic ester, $\text{CH}_3\text{COSCH}(\text{COOH})\text{CH}_2\text{COOH}$, which can be hydrolyzed to thiomalic acid.^{221, 301} Maleic anhydride may be used instead of the acid.⁸⁹ The sodium salt is formed by the addition of sodium hydrosulfide to sodium maleate.¹⁹⁵

The optically active thiomalic acids have been prepared.^{294a} Oxidation of the acid, or of its amide, does not change the direction of the rotation.^{379b} The structural relationships between the thiomalic and methylsuccinic acids have been investigated.^{222c}

The gold derivative can be prepared by heating the acid with

aurous cyanide.^{598a} Potassium^{598b} and sodium^{156, 263, 383, 457, 551} aurothiomalates have been extensively studied as therapeutic agents. The sodium salt protects mice against experimental hemolytic streptococcal infection,¹⁵² but does not cure it.⁴⁸⁰ It has been used to combat arthritis.^{73, 145, 225, 226, 274, 275, 460.} It combats *S. moniliformis*.²⁸⁰ Its effects on animals and the amounts of gold deposited in the various organs have been determined.^{73, 454} Its power is enhanced by the addition of sodium *p*-sulfamidobenzene aminomethylene sulfonate.⁴⁰⁴ Calcium auro-thiomalate has been used.^{73, 489b, 490} A diphenyl-arsenic derivative, $\text{Ph}_2\text{AsSCH}(\text{COOH})\text{CH}_2\text{COOH}$, m. 136° , has been reported.⁵⁷⁰ Alkali metal salts of antimonio-thiomalic acid are said to have therapeutic value.^{157, 441} The lithium antimony salt has been studied.^{181, 364, 441} Cysteine counteracts the toxic effects of this salt without diminishing its trypanocidal action.³⁷⁰ Thiomalic acid is useful for detecting palladium by spot test.³⁵¹

Spruce wood has been treated with thiomalic acid as with thioglycolic acid.^{293a}

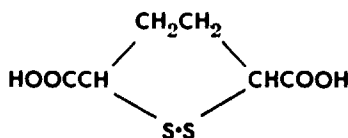
α -Thio- β -methylmalic acid, $\text{HOOC}\cdot\text{CH}(\text{SH})\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$, results from the hydrolysis of thiohydantoin- α -propionic acid.^{11d} The isomeric mercaptomethyl-succinic acid, $\text{HOOCCH}(\text{CH}_2\text{SH})\text{CH}_2\text{COOH}$, is known.^{512c} Mercaptomaleic acid, $\text{HOCC}(\text{SH})\text{:CHCOOH}$, has been prepared from bromomaleic acid.^{11d} Thiocitromalic acid melts at 116 to 118° .^{293a} Acetylthioitamic acid, from the addition of thioacetic acid to itaconic acid is saponified to thioitamic acid.³⁰¹

α -Mercaptoglutaric and α -mercaptopadipic acids have been prepared.²²¹ The intravenous toxicity to rabbits of mercaptoacetic acid is some ten times that of mercaptosuccinic or mercaptopadipic acid.^{151.5}

A mercapto-sulfo-succinic acid, $\text{HOOC}\cdot\text{CH}(\text{SH})\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{COOH}$, has been isolated from the reaction product of sodium thiosulfate and sulfuric acid on maleic acid.^{573, 574}

The addition of two molecules of thioacetic acid to acetylene dicarboxylic acid, followed by saponification, leads to dimercaptosuccinic acid.⁴⁴³ The toxicity has been compared with those of several other mercaptoacids. It gives definite protection against lewisite.^{151.5} α,α -Dimercaptodipic acid has been made

from dibromoadipic acid by the xanthate method. It can be oxidised to the cyclic disulfide,^{222a}

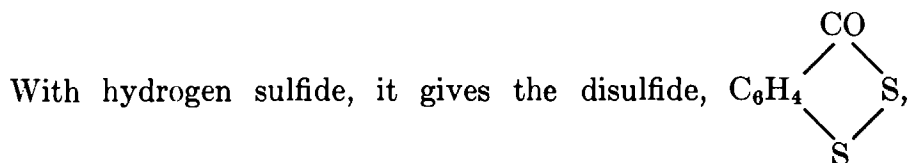


Aromatic Mercapto-Acids

Thiosalicylic acid, *o*-HSC₆H₄COOH, the most important of the aromatic mercapto-acids, has been prepared by the diazo reaction from anthranilic acid and sodium disulfide⁸ or xanthate.^{168, 200a, 290} It can be made by the reduction of benzenesulfinic acid with zinc and hydrochloric acid.²⁴³ The Kolbe synthesis has been adapted to its preparation. Sodium thiophenolate and carbon dioxide, under 36 to 50 atmospheres pressure at 150 to 190°, give thiosalicylic acid.¹¹⁴ It is obtained from thiophenol, carbon tetrachloride, and potassium hydroxide by a sort of Reimer-Tiemann reaction.³⁵⁶ *o*-Chlorobenzoic acid reacts with sodium sulfide and excess alkali at 170° in the presence of copper or copper salts.²⁴⁵ The formation of thiosalicylic acid starting with thiophenol and butyl lithium is of theoretical interest.²⁵⁰ A white modification, melting at the same temperature as the ordinary yellow form, has been reported.^{289, 543}

The reactions, as would be expected, are a combination of those of benzoic acid and of thiophenol. Its metal derivatives react with alkyl halides²⁸⁹ and with halo-acids such as iodoacetic acid.⁵⁴⁶ With an aryl halide, such as bromobenzene^{403a} or *o*-chlorobenzoic acid,^{403b} it is necessary to heat to 140 to 160° in the presence of copper powder. Condensation has been effected with α -chloroanthraquinone.⁵¹³

Amides and anilides can be prepared.³⁰⁵ The phenyl ester can be made from the acid, phenol, and phosphorus oxychloride.^{403a}



which can be reduced back to the original acid with zinc.⁵⁴³ This will be discussed again under cyclic sulfides.

Thiosalicylic acid precipitates heavy metal ions³⁵⁸ and has been recommended for the photometric estimation of iron in zinc and aluminum.¹⁸⁴

There has been much interest in the heavy metal derivatives of the salts and of the esters.⁴⁹² The gold salt, $\text{AuSC}_6\text{H}_4\text{COOK}$,^{200b} and the mercury salt, $\text{Hg}(\text{SC}_6\text{H}_4\text{COOK})_2$,⁴⁹¹ have been described. Mixed antimony salts, $\text{ClSb}(\text{SC}_6\text{H}_4\text{COOH})_2$ and $\text{Cl}_2\text{SbSC}_6\text{H}_4\text{COOH}$, are known.^{347, 629.5} The arsenic salt, $\text{As}(\text{SC}_6\text{H}_4\text{COOH})_3$,³⁴⁶ is a potent amebicide.²⁹¹ There is only one lead salt.³⁵ The nickel salt has been prepared.^{168.5} The diphenylarsenic derivative, $\text{Ph}_2\text{AsSC}_6\text{H}_4\text{COOH}$, is known.⁵⁷⁰ The gold, silver, arsenic, antimony, and bismuth derivatives of its esters are claimed as therapeutic agents.^{507a, 524} Methylmercury,^{339b} ethylmercury,⁴⁸⁵ dodecylmercury,⁴⁸⁵ and phenylmercury⁵¹⁸ derivatives, $\text{RHgSC}_6\text{H}_4\text{COOH}$, and the dicyclohexylgold compound, $(\text{C}_6\text{H}_{11})_2\text{AuSC}_6\text{H}_4\text{COOH}$,³⁴¹ and their salts have been investigated. The triethyl lead salt has been prepared.²⁵¹ The ethylmercury salt, $\text{EtHgSC}_6\text{H}_4\text{COONa}$, is slowly transformed into $\text{EtHgSC}_6\text{H}_4\text{COOHgEt}$ in the presence of air and sunlight.⁵⁷² Thiosalicylic acid replaces two of the phenyl groups of triphenylbismuth to form monophenylbismuth thiosalicylate.²⁵² It replaces one or more of the phenyl groups of the phenyl compounds of mercury, lead, tin, and bismuth to form salts.³⁵³

The 5-bromothiosalicylic acid has been made through the diazo acid from 5-bromoanthranilic acid.³⁵⁹ The 5-chlorothiosalicylic acid is obtained by reducing the disulfide which is produced by chlorinating thiosalicylic acid.²⁷³ The 4-amino-⁵⁵⁷ and 5-amino-thiosalicylic⁵⁵⁶ acids have been prepared. The ultraviolet spectrum of the former has been recorded.⁵⁵⁷ 4-Aminothiosalicylic acid has been made, starting with 4-nitroanthranilic acid.^{532.5} The 4-nitro acid, its ethyl ester, and its thioacetate are known.^{532.5}

m-Mercaptobenzoic acid, *m*- $\text{HSC}_6\text{H}_4\text{COOH}$, has been prepared through the diazo acid from *m*-aminobenzoic acid^{530, 629} and by reduction of the sulfone chloride.⁵⁴⁴ It forms mercaptide-salts similar to those of thiosalicylic acid.⁶²⁹ *p*-Mercaptobenzoic acid, *p*- $\text{HSC}_6\text{H}_4\text{COOH}$, like the meta isomer, has been made by the diazo reaction^{530, 590, 629} and by the reduction of the sulfone chloride.^{80, 542} The acid, *p*- $\text{HSC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, has

been obtained from the disulfide by reduction.^{188.5} 5-Mercaptosalicylic acid has been prepared by reducing the corresponding sulfone chloride with zinc and hydrochloric acid.⁵⁵⁹ When *o*-mercaptophenylacetic acid is treated with phosphorus pentoxide, thiooxindole is formed.²⁵⁴

Selenosalicylic acid and derivatives have been described.³³⁷

Amino-Mercapto-Acids

CYSTEINE, $\text{HSCH}_2\text{CH}(\text{NH}_2)\text{COOH}$

This is the simplest and also the most important of its class. It is the mercapto-acid corresponding to cystine, $(\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH})_2$, one of the building blocks of the proteins. Cystine is so important that a whole book could be written on it. It seems best to leave it out of this volume rather than to treat it inadequately. Cysteine will be discussed briefly without any attempt at completeness.

As cystine is so abundant, its reduction is the obvious way to prepare cysteine. In fact the reduction of cystine to cysteine and the oxidation of this back to cystine by Baumann was an important step in the understanding of cystine.³⁷ He used tin and hydrochloric acid, a method that has been a favorite ever since.^{12, 507b, 599.5} The reduction can be done catalytically over palladium⁵⁸ or by sodium in liquid ammonia.⁶⁰⁵ Cystine hydrochloride can be reduced by aluminum under certain conditions.⁴³⁶ Diformylcystine is reduced to formylcysteine by zinc.²⁴⁰ N-Methylcystine is reduced by sodium in liquid ammonia to N-methylcysteine.⁷² N-Methylcysteine and N-*i*-propylcysteine are made from 4-carboxythiazolidines by reduction with sodium in liquid ammonia.^{135b}

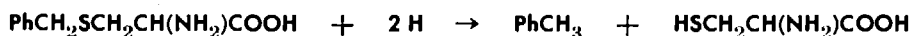
Cysteine has been synthesized in a number of ways. One of the most direct is the addition of a thioacid to α -acylaminoacrylic acid, followed by hydrolysis: ^{46, 176b, 201, 202, 522}



Another method is the addition of benzyl mercaptan to α -chloroacrylonitrile:



The chlorine is replaced by the amino group and the nitrile saponified.²⁶² The reason for using benzyl mercaptan is that the benzyl group can be split off by sodium in liquid ammonia: ⁴³⁵



Benzyl mercaptan may be added to hexylideneaminoacrylic acid.¹⁴² An earlier synthesis started with β -chloro- α -aminopropionic acid and barium sulfhydrate.²⁰⁸ In another synthesis an ester of benzoylserine was treated with phosphorus pentasulfide.^{191, 192} To account for its formation in plants, it has been assumed that mercaptoacetaldehyde, from formaldehyde and thioformaldehyde, might combine with hydrocyanic acid.²²⁰

Cysteine being both an acid and an amine exists as an inner salt and, as a salt, has a high and indefinite melting point. As it has three active groups it has the characteristic reactions of all three. Its conduct as an aminoacid need not be considered here. Its absorption spectrum has been compared to those of several other aminoacids.¹⁴

As a mercaptan it undergoes oxidation to cystine, the corresponding disulfide. The oxidation potential has been measured.^{164, 247, 338, 631} The cystine-cysteine equilibrium is believed to be of great importance in many life processes. Cysteine is oxidised rapidly by atmospheric oxygen, but only within a narrow pH range around neutrality. As a positive or negative ion it is relatively stable.³⁹⁹ The autooxidation of specially purified cysteine is extremely slow.⁴⁹³ It is catalyzed by metals.⁶¹⁶ Iron, copper, mercury, and arsenic favor the oxidation; lead, nickel, copper, uranium, thorium and cadmium oppose it.¹ The presence of an organic disulfide helps.¹⁶⁵ It is inhibited by hydrocyanic acid ^{1, 272a, 399, 593} and by some nitriles.^{399, 593} Copper ^{38, 593} and iron ^{191, 271, 493, 593} are specially active. One tenth of a gamma of iron is effective.^{272a} The oxidation by hydrogen peroxide in hydrochloric acid solution goes at a measurable rate.⁵⁹⁴ It can be followed by the change in rotation.^{519b} The rate of oxidation by hydrogen peroxide at pH 2.1 in the presence of copper is proportional to the concentration of the copper and of the peroxide, but with iron it is proportional to the concentrations of the iron and of the cysteine.^{455b} In the oxidation by hydrogen peroxide in the presence of thiourea, dithioformamidine is supposed to be an intermediate.^{455d} Cysteine is oxidised by Folin's uric acid

reagent in neutral solution when copper ions are present.¹⁵ The oxidation by iodine may go all the way to cysteic acid.^{65, 536a} Oxidation by nitric acid gives isethionic acid.⁴³⁰

Cysteine forms complexes or salts with silver,⁶⁰⁰ lead,³⁵ zinc,¹⁸⁸ iron,^{411, 525b} cobalt,^{85b, 413, 525a, 525c} nickel,^{85b} copper,^{455a} arsenic,³⁶³ and diphenylarsenic.⁵⁷⁰ In alkaline solution, ketene acetylates both the mercapto and the amino groups of cysteine^{431, 452, 456} or its ethyl ester.¹¹⁸ An aldehyde reacts with the amino and the mercapto groups to form a thiazolidine.^{246, 286, 465} Acetone acts similarly.⁶³⁷ The mercaptal, $\text{H}_2\text{C}(\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH})_2$, is obtained from cysteine and methylene chloride in liquid ammonia.^{603, 609} This has been proved to be identical with djenkolic acid⁶⁰⁹ isolated from the djenkol bean.²⁸⁷ There has been disagreement about the composition of the reaction product of cysteine with selenous acid.^{444, 555} It appears to be $\text{Se}[\text{SCH}_2\text{CH}(\text{NH}_2)\text{COOH}]_2$.³⁴⁸ Cysteine can be esterified in the usual way, with an alcohol and hydrogen chloride.⁴⁶¹ It gives a color test with nitroprusside sensitive to 1 in 60,000⁵⁰¹ and a red color with nitrous acid,^{592b} but the most distinctive reaction is the one with sodium 1,2-naphthoquinone-4-sulfonate.⁵⁶⁵ Cysteine can be added to an unsaturated lactone¹¹⁰ and to phenyl vinyl sulfone.²¹⁴ It has been used in the synthesis of peptides.^{342.5}

The most curious thing about cysteine is the ease with which it is decomposed. Hydrogen sulfide is supposed to be lost from the enol form: ⁴³³



When cysteine is boiled in pure water, some hydrogen sulfide and ammonia are given off and cystine is formed. The reactions are complex.⁴⁸³ With alkaline plumbite solution, pyruvic acid is formed.¹²¹ Such a cleavage of a sulfur-carbon bond is quite unusual.⁵⁷⁷

HOMOLOGS AND ANALOGS

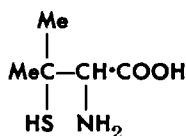
Next to cysteine comes homocysteine, $\text{HSCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$. The chief interest in this is its relation to methionine, its methyl derivative, $\text{MeSCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$. Refer to the section on methionine in the chapter on sulfide acids. Homocysteine can be prepared by the cleavage of the benzyl derivative, $\text{PhCH}_2\text{SCH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, by sodium in al-

cohol. Heated with an acid, it forms a thiolactone⁴⁷⁵ which is opened by alkali.⁶¹⁰ It adds to an unsaturated lactone.¹¹⁰ The dissociation constant has been determined by electrometric titration.^{487b} This can be done polarographically with the aid of cobalt ion.⁵⁵⁸ Hydrogen sulfide is eliminated from it by certain enzymes. There has been much interest in its metabolism and utilization by animals in comparison with cystine and methionine.^{82, 237, 476, 625}

The isomeric α -mercapto- γ -aminobutyric acid, $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}(\text{SH})\text{COOH}$, has been prepared by the hydrolysis of the phthalimino compound.²⁴¹ Several other mercapto-amino-acids of this type have been prepared by methods more or less similar. Some of these are: β -methylcysteine, $\text{HSCHMeCH}(\text{NH}_2)\text{COOH}$,^{106, 108} β -ethylcysteine, $\text{HSCHEtCH}(\text{NH}_2)\text{COOH}$,^{144, 148} β -methyl- β -ethylcysteine, $\text{HSCMeEtCH}(\text{NH}_2)\text{COOH}$,^{106, 148, 611} β , β -diethylcysteine, $\text{HSCEt}_2\text{CH}(\text{NH}_2)\text{COOH}$,^{106, 611} β -*i*-propylcysteine, $\text{HSCH}(\text{CHMe}_2)\text{CH}(\text{NH}_2)\text{COOH}$,¹⁴⁸ α -amino- γ -methyl- γ -mercaptopaleric acid¹⁰⁹ and ϵ -benzoylamino- α -mercaptocaproic acid.²⁵⁸

The β , β -dimethylcysteine, known as penicillamine, is so important that a whole section will be devoted to it.

PENICILLAMINE



This is β , β -dimethylcysteine, or β -mercaptopaleric acid. It is of interest from the fact that it is an important part of the penicillin molecule. For information beyond what can be given in this brief sketch, reference must be made to the massive volume on penicillin by H. T. Clarke and associates.¹²² This includes a history of penicillamine.¹²³

The first isolation was by the hydrolysis of barium penicillin by 0.1 *N* sulfuric acid. It was obtained as the mercury derivative. It was shown to be a primary amine containing a strong and a weak acid group. The first formula given was $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$ as the presence of sulfur was not suspected and the oxygen was determined by difference.³ It has been isolated from other penicillin products.^{2, 135a, 158, 159, 260, 406, 450a, 634, 635}

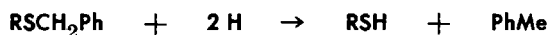
Syntheses

The various syntheses of penicillamine are given in detail in the penicillin monograph¹⁴⁸ to which reference should be made. The problem is to get the mercapto and amino groups into the proper position in isovaleric acid.

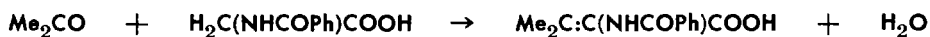
On paper, nothing could be simpler than the addition of hydrogen sulfide to α -amino- β,β -dimethylacrylic acid:



Some day, perhaps, it will be done directly instead of in round-about ways as at present. As hydrogen sulfide is inconvenient to handle and does not add readily to unsaturates, benzyl mercaptan is used instead. This mercaptan is chosen since benzyl sulfides are cleaved readily by sodium in liquid ammonia: 10b, 98, 136, 137, 215, 331.5, 428, 429, 500, 563a, 564, 579, 584, 608



The amino group of the amino acid is commonly acylated for its protection and this product converted to the oxazolone. It so happens that acetone condenses with hippuric acid: 2, 408b, 534a



This condenses to 2-phenyl-4-isopropylidene-5(4)-oxazolone.^{408b, 422, 534a} One synthesis, of which there are numerous variations, starts with the addition of benzyl mercaptan to this oxazolone.^{2, 98, 140, 400, 408b, 428, 429, 500, 534a, 580, 581, 584.5} To avoid the odor, sodium benzyl thiosulfate may be substituted for the free mercaptan.⁸⁷ Mild hydrolysis of the addition compound gives N-benzoyl-S-benzyl-DL-penicillamine, from which the benzoyl group may be removed, leaving S-benzylpenicillamine which is then cleaved. α -Acetamino- β,β -dimethylacrylic acid may be substituted for the α -benzoylamino acid. This has the advantage that its oxazolone is more reactive.^{187, 563a, 564} It is claimed that it reacts with hydrogen sulfide.²⁴ The acetamino acid can be used without conversion to the oxazolone.^{563a, 564, 583, 584}

S-Benzylpenicillamine can be obtained by the addition of benzyl mercaptan to α -nitro- β,β -dimethylacrylic acid, or ester, and reduction of the nitro group.^{10a, 10b, 136, 137, 597} The addition of thioacetic acid to α -acetylamino- β,β -dimethylacrylic acid gives

the thioacetate, $\text{Me}_2\text{C}(\text{SAc})\text{CH}(\text{NHAc})\text{COOH}$, which is converted to penicillamine by simple hydrolysis.^{423a} Thioacetic acid may be added to α -nitro- β,β -dimethylacrylic ester which is then reduced and hydrolyzed.^{563a}

Conditions have been found under which hydrogen sulfide can be added to the oxazolone. This saves one step in the synthesis.^{140, 148, 244, 439}

An ester of α -amino- β,β -dimethylacrylic acid and carbon disulfide unite almost quantitatively to give the ester of 2-thio-4-carboxy-5,5-dimethylthiazolidine. The ester is hydrolyzed, the thiazolidine cleaved by reduction, and the acid isolated.^{51b, 68, 148, 278, 533} From suitably substituted thiazolidines, various N-substituted compounds can be prepared.^{148, 278}

The Strecker synthesis starts with the aldehyde, $\text{PhCH}_2\text{SCMe}_2\text{CHO}$, to which hydrocyanic acid is added. The hydroxyl of the cyanhydrin, $\text{PhCH}_2\text{SCMe}_2\text{CH}(\text{OH})\text{CN}$, is replaced by the amino group and the nitrile hydrolyzed. Finally the benzyl group is eliminated.^{148, 279, 582, 588}

REACTIONS

The reactions are those appropriate to the three active groups, carboxyl, amino, and sulfhydryl, though the activity of each is somewhat modified by the presence of the others. The reactions are practically the same as those of cysteine, though modified by the tertiary character of the sulfhydryl group. This reacts normally with methyl iodide⁵⁰⁰ and other alkyl halides.

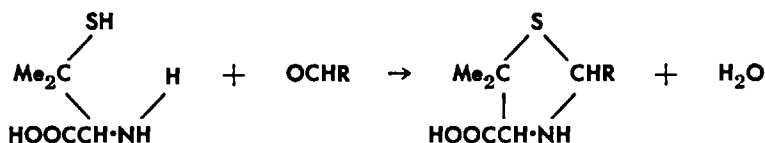
Oxidation to the disulfide is effected by iodine,^{2, 53, 99} hydrogen peroxide,⁵³ or air.^{2, 53, 439} There are two forms of the disulfide, melting at 212 to 215° and 169 to 171°.⁹⁹ The oxidation is less easy than that of cysteine.¹⁴⁸ There is the same difference between *t*-butyl mercaptan and *n*-butyl. Oxidation with bromine^{2, 148, 450a} or hydrogen peroxide¹⁴⁸ may give the sulfonic acid.

It is usual to tie up one or both of the other groups before esterification of the carboxyl. Introducing the formyl group takes care of the amino,⁴²⁹ while the reaction with acetone inactivates both the amino and the sulfhydryl.^{139, 622} The protecting groups are then eliminated from the esters. Esterification can be effected without protecting these groups.^{329, 408a, 534b} Penicillamine esters have antibacterial properties *in vitro* but the action is not related to that of penicillin.⁹⁰

In order to restrict the action of an acid chloride to the amino group, the sulfhydryl is blocked. S-Benzyl-N-caproylpenicillamine, m. 131° , is made by treating the S-benzyl derivative with caproyl chloride.^{135a} Other acyl derivatives are made similarly.^{45, 142}

Penicillamine phenyl ureide is desulfurized by Raney nickel.^{450a} In the conversion of S-benzyl-L-penicillamine by "deuterized" Raney nickel to L-valine, the uptake of deuterium is 1.6 atoms.³²⁸

A characteristic of penicillamine and of its esters is the condensation of an aldehyde, or a ketone,^{51a, 135b, 148, 587b} to form a 4-carboxy-5,5-dimethyl thiazolidine:



An acetal may be substituted for an aldehyde.^{52, 88, 135b, 140, 587b} Condensations have been effected with formaldehyde^{315, 428, 429, 439, 563b, 624} and several other aldehydes.^{135b, 141, 421, 563b, 587b, 606} The 2,2,5,5-tetramethyl-4-carboxythiazolidine, often called isopropylidene penicillamine, from the condensation with acetone has been particularly useful in syntheses as mentioned under esterification.^{139, 622} Once the group has been put in, the acetone is hydrolyzed off, leaving the penicillamine with the desired substituent. The isopropylidene derivative is convenient for isolating and purifying penicillamine. It is hydrolyzed quantitatively by heating with water.^{2, 534a, 564, 587a, 630}

By starting with N-phenylacetylglutamic acid, N(N-phenylacetyl)- α -DL-glutamyl-D-penicillamine has been prepared.²⁷

The methyl ester of penicillamine condenses with carbon disulfide to the ester of 2-marcapto-5,5-dimethyl-2-thiazoline-4-carboxylic acid.¹³³ The ethyl ester condenses with thioacetamide to the ester of 2,5,5-trimethyl-4-carboxythiazoline.¹³²

Penicillamine enters into a variety of condensations.^{19, 28, 106, 107, 123, 131, 133, 134, 135a, 136, 137, 140, 149, 402, 421, 439, 450b, 534b, 563b, 563c, 564, 607a, 607b, 612, 638} Some of these have been used in attempts to synthesize penicillin.

When S-benzylpenicillamine is heated with urea, it replaces one of the amino groups to give $\text{PhCH}_2\text{SCMe}_2\text{CH}(\text{NHCONH}_2)\text{COOH}$.⁵⁷⁸

Penicillamine gives deep red-violet color with sodium nitroprusside in alkaline solution, and a bluish purple with ninhydrin.² Penicillamine is determined colorimetrically, using Nessler's reagent.¹⁵⁸ The formation of the mercury derivative with mercuric chloride has been important in the detection and isolation of penicillamine and of other penicillin compounds in which the sulfhydryl group is open.^{3, 148, 421, 423a, 450b, 634}

The resolution of the racemic synthetic penicillamine is accomplished by means of the alkaloid salts of the N-formylisopropylidene derivative^{174, 623} or of the N-formyl-S-benzyl derivative.^{2, 148, 423b} The D-isomer is obtained by racemizing the derivative of the L-isomer and separating as an alkaloid salt.^{175, 608} Natural penicillamine has the "unnatural" D-configuration as proved by the conversion of its phenylcarbamyl derivative to D-valine phenyl ureide by desulfurizing with Raney nickel.^{450b}

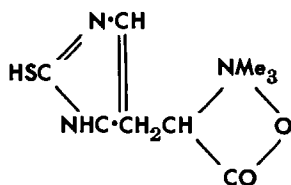
The infrared spectra of penicillamine and the methyl esters of its N-acetyl derivative and of its N-acetyl-S-benzyl derivative have been recorded.⁵⁹¹ Crystallographic x-ray studies have been made of active and racemic penicillamine hydrochlorides and of several of their derivatives.¹⁵⁰ The pK values for the three ionizable groups are $-\text{CO}_2\text{H}$ 1.8, $-\text{NH}_2$ 7 and $-\text{SH}$ 10.5.²

Various compounds have been synthesized and considered as possible precursors in the biosynthesis of penicillin.^{44, 143} The S-propylpenicillamine has been made by the addition of propyl mercaptan to the oxazolone as in the synthesis of S-benzylpenicillamine.⁵⁶⁰ α -Amino- β -mercapto- β,β -pentamethylenepropionic acid has been obtained by the hydrolysis of the corresponding thiazoline.⁶⁸

S-Benzylpenicillamine has been compared with a number of other aminoacids in a study of the enzymic synthesis of peptides.²¹⁶

The effects of the decomposition products of penicillamine on photographic emulsions have been studied.³⁵²

ERGOTHIONEINE



This is listed in *Chemical Abstracts* as *thioneine*. In this tautomeric form, it is a mercaptan, so it is placed here with mercapto acids.

It was first isolated from ergot of rye,⁵⁷⁵ 1 kg. of which yielded 0.65 g.¹⁸² It has been obtained from ergot of diss, a wild grass from East Algiers.⁵⁷⁶ Ergots of various plants have been examined for their ergothioneine content, which ranges from 0.157 to 0.531%. The average for ergot of barley is 0.376% and for that of rye 0.336%.³¹³

It was subsequently isolated from blood, but regarded as a new substance and given the name thiasine.^{48, 50, 312a} "Sympectothion" from pigs' blood was found to be the same.^{312b} Later the identity of the substance from these diverse sources was established.^{183, 432} Its presence in blood is general,^{31, 42, 261} the amount ranging from 3 to 12 mg. per 100 cc. of corpuscles.⁴⁹⁶ Directions for its isolation from either source have been given.³¹⁴ It is obtained as a copper compound.^{455c, 632}

A substance resembling ergothioneine has been isolated from urine.⁵⁶⁶

When ergothioneine is boiled with aqueous potassium hydroxide, trimethylamine is evolved and β -2-thiolglyoxaline-4-acrylic acid is formed. This indicated the structure given before³² and led to attempts at synthesis.³¹ The synthesis has been accomplished in stages. The 2-mercapto derivative of desaminohistidine was put together by heating the hydrochloride of the aldehydo-acid, $\text{OHCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COOH}$, with ammonium thiocyanate.⁶ Similar treatment of α,δ -diamino-ketovaleric acid gave the mercaptohistidine.^{17, 163, 270} It remained to convert this to the betaine which was accomplished by methylating the amino group with methyl iodide and silver oxide, after protecting the mercapto group.²⁷⁶

As an amino acid it forms salts with either strong bases or strong acids. In the free state, it is an inner salt. As a mercaptan it forms mercaptides. The complexes containing mercury¹⁸² or copper,^{455c, 632} which have been useful for its isolation, may be considered as mercaptides.

As was mentioned before, trimethylamine is evolved when it is heated with alkali. Treatment with an acid gives hydrogen sulfide.⁵⁷⁵

The temperature affects the uptake of iodine as it does with

cysteine.³⁹³ Electrometric titration shows the three groups, mercapto, amino, and carboxy.⁴⁷² The oxidation potential is 0.36 volts and the free energy 16,600 cal. compared to 0.32 and 14,800 for thiolhistidine.^{487a}

Ergothioneine shows no distinctive pharmacological action when administered to a rabbit or a cat.⁵⁶⁹

Tungstic, molybdic,⁴³ tungstomolybdic⁴⁰ and iodobismuthous^{372a} acids are used to precipitate ergothioneine from blood. The red color which ergothioneine gives with diazotized sulfanilic acid is useful for its estimation.^{311, 372a 372b} A micro method is based on the use of a ferricyanide.²¹¹ The sulfur may be converted to the sulfate ion by bromine.⁵⁹⁶ Ergothioneine is one of the compounds that catalyze the decomposition of sodium azide by iodine.^{233b} Ergothioneine may be detected in biological fluids and determined approximately by chromatographic methods.^{630, 640} Selective absorption bands in the ultraviolet²⁹² may be used for its detection.⁵⁴⁰

Physical Properties of Mercaptoacids

The physical properties of a number of mercaptoacids are brought together in the following pages. Reference should be made to the remarks in the introduction to similar data in Chapter 1.

The atomic refraction of sulfur in the mercapto acids is 7.71 and appears to be independent of the relation of the sulphydryl group to the carboxyl group. In the acetyl derivatives, the value is 8.44 and in the lactones, 8.13.^{512b} The molecular diamagnetic susceptibility of thioglycolic acid is 49.96 compared with the calculated 50.25.¹²⁶ Its Raman spectrum shows a strong continuous background with strongest lines at 814 and 1409.⁵⁸⁶ The optical properties of several of these acids have been investigated by Levene and Mikeska.^{379a, 379b, 379c} The dissociations have been measured by Ostwald and several others.^{101, 368a, 440, 617} The specific heats from 85 to 300°K and entropies have been measured for L-cysteine and β-thiolactic acid.³⁰⁹

MONOBASIC MERCAPTO-ACIDS

HSCH₂COOH, m. -16.5°; ³⁴⁵ b₁₃ 102.5-3°; ^{66b} b₁₄ 103-5°; ^{66a} b₁₆ 107-8°; ^{345, 526} b₂₀ 95-7°; ⁴⁸¹ b₂₉ 123°; ^{66a} d_{17.3} 1.326; ^{66b} d₂₀

1.3253; ³⁴⁵ K_1 4×10^{-4} , K_2 1×10^{-10} ; ¹⁰¹ K_1 2.1×10^{-4} , K_2 2×10^{-11} ; ^{368a} K 0.0225.⁴⁴⁰

Me, b_{16} 49–51°. ⁵⁵²	$C_{10}H_{21}$, b_8 148–50°. ⁴²⁶
Et, b_{17} 55°. ³⁴⁵ b_{20} 63°; ²⁶	$C_{12}H_{25}$, b_3 170–1°. ⁴²⁶
d_{15} 1.0964. ³⁴⁵	$C_{14}H_{29}$, m.35°. ⁴²⁶
<i>i</i> -Pr, b_{10} 51°. ⁴²⁶	$C_{16}H_{33}$, m.44.5°. ⁴²⁶
Bu, b_2 63–6°. ⁴²⁶	$C_{18}H_{37}$, m.52.5°. ⁴²⁶
<i>i</i> -Bu, b_8 60°. ⁴²⁶	PhCH ₂ , b_3 121–3°. ⁴²⁶
Hex, b_7 103–5°. ⁴²⁶	PhCH ₂ CH ₂ , b_3 134°. ⁴²⁶
	<i>c</i> -Hexyl, b_8 102–3°. ^{617.5}

Amide, m.52°; ³⁴⁵ anilide m.114°; ^{525e} 110°; ^{283a} toluides: *o*-, m.85°; *m*-, m.153°; ^{39a} *p*-, m.126°; ^{38a}, ^{283a} anisidine, m.116°; phenetidine, m.117°; ^{39a} β -naphthalide, m.112°.⁵⁷

Ac., $b_{2.5}$ 115–8°; ⁶²¹ b_{13} 149–50°; ^{435.5} b_{17} 158–9°; ⁴⁷ Bz., m.108°; ^{294e} 106°; ^{244.5} trichloroacetyl, Et, b_2 122–3°.^{275.5}

HSCHMeCOOH, b_{14} 99°; ^{66b} b_{16} 102°; ²²¹ 95–100°; ^{379a} b_{19} 118–22°; ^{66a} n 16/D 1.4823; ²²¹ K_1 2.0×10^{-4} ; K_2 2.0×10^{-11} ; ^{368a} L -, b_{15} 99–101°; $d_{19.2}$ 1.193; $[\alpha]$ –45.5; D -, 45.5°; ^{391d} 49.9°; ^{332b} anilide, m.91°; ^{39a} Ac., b_1 132–3°; ³⁴¹ Et, b_3 55°; n 19/D 1.4625.²²¹

HSCMe₂COOH, m.47°; b_{15} 102°; ^{66b} K_1 1.26×10^{-4} ; K_2 0.48×10^{-11} .^{368a}

HSCHEtCOOH, b_{16} 118–20°; ^{66a} b_{22} 123–8°; ⁵¹¹ anilide, m.95°; ^{39a} toluides: *o*-, m.99°; *m*-, m.72°; *p*-, m.78°.^{39b}

HSCEt₂COOH, m.28.5°; b_5 113–7°; d_{25} 1.0718; n 25/D 1.4768.^{205.5}

HSCHPrCOOH, $b_{0.8}$ 84–5°; d 20/4 1.0938; n 20/D 1.4752.^{512b}

HSCHBuCOOH, b . 234°.⁴³⁴

HSCH(C₆H₁₃)COOH, oil.¹⁸⁶

HSCH(C₇H₁₅)COOH, m.33°; $b_{0.9}$ 140–5°.⁵¹¹

HSCH(C₈H₁₇)COOH, m.47°.¹⁸⁶

HSCH(C₉H₁₉)COOH, m.50°; b_{18} 165–6°.⁵¹¹

HSCH(C₁₀H₂₁)COOH, m.59°.^{186, 434}

HSCH(C₁₂H₂₅)COOH, m.66°.^{186, 434}

HSCH(C₁₄H₂₉)COOH, m.73°.^{186, 434}

HSCH(C₁₆H₃₃)COOH m.80°; ^{186, 434} 74°; ¹⁸⁵ 70.5°.⁵¹¹

HSCH(CH₂Ph)COOH, m.46°; b_{11-12} 184–7°.⁶⁷

HSCH₂CH₂COOH, m.16.8°; ^{66b} b_3 85–6°; ^{255, 259, 301} b_5 85°; ²²¹ b_{13} 117–22°; ²⁵ b_4 105–7°; ¹¹⁷ b_{15} 111°; $d_{20.8}$ 1.218; ^{66b} d 20/4 1.2199; n 20/D 1.4921; ³⁰¹ 1.4910; ¹¹⁷ n 25/D 1.4918; ²²¹ K_1

- 0.46×10^{-4} , K_2 2.9×10^{-11} ; ^{368a} heat of combination constant pressure 54,500 cal.; entropy 25° 54.7, ΔF -82,220 cal.; ³⁰⁹ Me, b_{13} 64-5°; ²⁵ b_{14} 54-5°; ¹⁷⁰ n 19/D 1.4628; ¹⁷⁰ Et, b_{20} 76-8°; ¹⁰³ Ac., m.52-4°; ³⁰¹, ^{435.5} b_3 127-8°; ³⁰¹ Me, b_5 68°; n 17/D-1.4773.²²¹
- HSCHMeCH₂COOH, $b_{2.5}$ 87-8°; ³⁰¹ b_{10} 111°; ³²⁴ 116-8°; ^{379c} b_{20} 124-7°; ¹⁹⁵ d 20/4 1.1371; n 20/D 1.4782; ³⁰¹ $[\alpha]$ 20/D -41.05, Na, $[\alpha]$ 20/D -14.86; ^{379c} Me, b_{12} 80°; ⁵⁰⁴ Et, b_{50} 95-110°; ³⁷⁴ Bu, b_{10} 110°; ^{114.5} anilide, m.91°; toluides: *o*-, m.99°; *m*-, m.72°; *p*-, m.75°; ^{39b} Ac., b_3 129-30°; d 20/4 1.1755; n 20/D 1.4902. ³⁰¹
- HSCH₂CHMeCOOH, b_{12} 120-2°; ^{369d} Ac., m.40.5; Me, b_{103} .²²³
- HSCHEtCH₂COOH, b_4 108-10°; d 20/4 1.1014; n 20/D 1.4784; Ac., m.43-5°; b_2 133-4°.^{512b}
- HSCMe₂CH₂COOH, m.38°; ^{563a} 35°; b_{10} 112-5°; ²¹³ b_{12} 118-20°; Ac., b_{14} 145-8°.^{563a}
- HSCHPhCH₂COOH, m.112.5°; ²⁰⁷, ³⁰¹ Ac., m.96°.³⁰¹
- HSCH₂CH₂CH₂COOH, $b_{2.5}$ 103°; d 20/4 1.1630; n 20/D 1.4912; Ac., b_3 138.5-9°; d 20/4 1.1864; n 20/D 1.4949; ³⁰¹ lactone, b_{20} 90-2°.^{19.5}
- HSCHMeCH₂CH₂COOH, $b_{0.05}$ 90-1°; d 20/4 1.1020; n 20/D 1.4802; ^{512b} ureide, m.186°; ³²⁵ lactone, b_8 85-6°, b_{214} -6°; d 20/4 1.0975; n 20/D 1.5028; Ac., b_3 133-4°; d 20/4 1.1394; n 20/D 1.4880.^{512b}
- HSCMe₂CH₂CH₂COOH, b_{10} 110°.⁵⁴⁷
- HSCHEtCH₂CH₂COOH, lactone, b_8 100-1°.^{512a}
- HS(CH₂)₄COOH m.25°; $b_{0.8}$ 110-2°; d 20/4 1.1195; n 20/D 1.4882; ^{512a} lactone b_{25} 150-2°; ^{19.5} b_{12} 106-7°; ^{512a}, ^{512b} d 20/4 1.1553; n 20/D 1.5317; ^{512a} SAc., m.54°.^{512b}
- HS(CH₂)₅COOH, b_{13} 155-6°.³¹⁸
- HS(CH₂)₁₀COOH, m.51°; ⁴⁶⁴ 47°; ¹²⁷ 95°.³⁶
- HSCH:CHCOOH, Ac., *trans*, m.150°; Me, *trans*, $b_{0.5}$ 73°; m.84.5°; *cis*, m.58.5°.⁴⁴³
- HSCMe:CHCOOH, Me, b_{12} 68-9°; d 29.5/4 1.1124; n 20/D 1.5222; Et, b_{18} 77°; d 29.5/4 1.0747; n 20/D 1.53749.⁵⁰⁶
- HSCHPh:CHCOOH, m.110°.²⁰⁷
- Mercaptoelaidic, Me, m.31°.⁴⁹⁴
- Mercaptoelaidic, m.70°.⁴⁹⁴
- HSCH₂CH(OH)COOEt, b_{19} 113-5°; d 25/4 1.1745; n 25/D 1.4754.³⁵⁰
- HSCH₂CHClCOOMe, Ac., b_1 72°; n 25/D 1.4898.³⁷³, ⁴⁴⁹

HSCHMeCOCOOH, m.190°. ^{447b}

PhO(CH₂)₃CH(SH)COOMe, b₁ 138–42°. ²⁶

HSCH₂C(OH):C(CN)COOEt, Ac., m.71°. ⁴⁷

ClC₆H₄O(CH₂)₃CH(SH)COOMe, b₁ 155–8°. ²⁶

DIMERCAPTO-ACIDS

(HSCH₂)₂CHCOOH, m.62°. ^{321, 322}

HSCH₂CH(SH)COOH, m.74.5°; Me, b_{0.2} 40°; d 25/4 1.2294; n 25/D 1.5251; ^{373, 449} diAc., b_{0.001} 83–4°; n 22/D 1.5201. ⁴⁴³

HSCH₂CH(SH)CH₂COOH, diAc., Et, b₁ 147–8°; n 20/D 1.545; δ-mercapto-γ-valerolactone, b_{0.2} 83–4°; n 17/D 1.5630. ¹⁹⁸

HSCH₂CH(SH)CH₂OCH₂COOH, b_{0.0001} 150°; n 23/D 1.5505; diAc., b_{0.4} 147°; n 10/D 1.5098. ¹⁹⁸

HSCH₂CH₂CHSH(CH₂)₄COOH, b_{0.7} 161.5°; n 25/D 1.5233. ^{466.5}

HSCH₂CH(SH)(CH₂)₈COOH, b_{0.2} 166–7°. ⁴⁴⁹

DIBASIC MERCAPTO-ACIDS

HSCH(COOH)₂, m.83°. ^{512a}

HSCH(COOH)CH₂COOH, m.151°; ^{221, 294a, 301} 150°; ^{479, 571} 148°; ^{66a} 155°; ¹⁹⁵ DL-, m.150°; L-, m.153°; [α] 17/D–75.8°; D-, m.153°; [α] 17/D 76.1°; ^{294a} K 0.0523; ⁴⁷⁹ D-amide-acid, m.125°; [α] 18/D 82.5; ²⁹⁸ Et, b₁₄ 63°; ²²¹ b.246° decomposes; ⁴⁷⁹ Ac., m.126°; ^{330, 435.5} anhy., m.71–3°; ³⁰¹ 77°. ⁸⁹

HSCMe(COOH)CH₂COOH, thiocitramalic, m.118°; ^{293d} Ac., m.123.5. ³⁰¹

HSCH(COOH)CH₂CH₂COOH, α-mercaptoglutaric, m.97°; Ac., Et, b₁₅ 178–9°; n 20/D 1.4727. ²²¹

HSCH₂CH(COOH)CH₂COOH, thioitamic, m.108.5°; lactone, m.110°; Ac., m.91.5°. ³⁰¹

HSCH(COOH)(CH₂)₃COOH, α-mercaptoadipic, m.113°; ²²¹ Me, b₁₈ 154–7°; ²⁵ Ac., Et, b₁₂ 177°; n 17/D 1.4680. ²²¹

HSCH(COOH)CH(SH)COOH, dimercaptosuccinic, m.192°; diAc., m.171–3°; Me, m.120°. ⁴⁴³

HSCH(COOH)(CH₂)₂CH(SH)COOH, α,α'-dimercaptoadipic, MESO, m.185°; D- or L-, m.195°; DL, m.112.5°. ^{222a}

HSCMe₂CH(COOH)₂, m.137°; di Et, b₁ 90–3°. ²¹³

HSCH₂(CH₂)₂CH(COOH)₂, m.82.3°; Ac., m.94.5°. ^{512a}

AROMATIC MERCAPTOACIDS

o-HSC₆H₄COOH, m.165°; ^{289, 543} 168°; ^{336.5} 177°; ³⁵⁶ Me, b.242°; ²⁴³ b₁₋₂ 115–9°; ^{336.5} b₂ 98–100°; d 25/4 1.2191; n 25/D 1.5911; ^{205.3}

- Ph, m.91°; ^{403a} anilide, m.237°; toluides: *o*-, m.218°; *p*-, m.230°; *o*-aniside, m.157°; naphthamide, α -, m.248°; β -, m.168°.³⁰⁵
- m*-HSC₆H₄COOH, m.147°;⁵⁴⁴ 146°;^{336.5} 145°;⁶²⁹ Me, b₁₁ 135–6°;⁵³⁰ 126–31°; Et, b₁₁ 147–9°.⁶²⁹
- p*-HSC₆H₄COOH, m.220°;^{336.5} 219°;^{590, 629} 217°;⁸⁰ Me, m.56°;^{336.5} 50°;⁵³⁰ 47°; b₁₁ 139–44°;⁶²⁹ 139–40°;⁵³⁰ anilide, m.264°; β -naphthamide, m.283°.³⁰⁵
- o*-HSC₆H₄CH₂COOH, m.97°.²⁵⁴
- 2,5-HS(Me)C₆H₃COOH, m.82°.³⁵⁶
- 3,2-HSC₁₀H₆COOH, anilide, m.286°; toluides, *o*-, m.280°; *p*-, m.277°; *o*-aniside, m.221°; α -naphthamide, m.307°.³⁰⁵
- 1,8-HSC₁₀H₆COOH, lactone, m.146°;³⁰⁵ 145°.⁴⁸⁵
- 2,4-HS(Cl)C₆H₃COOH, m.196°.^{336.5}
- 2,5-HS(Cl)C₆H₃COOH, m.194°;^{336.5} 193°;²⁷³ 110°;³⁵⁶ Me, m.45°.^{336.5}
- 2,3,5-HS(Cl₂)C₆H₂COOH, m.208°;^{577.5} 198°.^{336.5}
- 2,3,6-HS(Cl₂)C₆H₂COOH, m.122°.³⁵⁶
- 2,5-HS(Br)C₆H₃COOH, m.211°;^{336.5} 183°.³⁵⁹
- 2,3,5-HS(Br₂)C₆H₂COOH, m.222°; Me, m.89°.^{336.5}
- 4,2-HS(HO)C₆H₃COOH, m.205°.^{442.5}
- 5,2-HS(HO)C₆H₃COOH, m.245°;³⁵⁹ 152°.⁵⁵⁹
- 2,4-HS(NH₂)C₆H₃COOH, m.198°;^{532.5} 197°;^{4.5} HCl, m.220°;^{532.5} Ac., m.299°;^{532.5} 137°;^{4.5} Et, m.198°.^{532.5}
- 2,5-HS(NH₂)C₆H₃COOH, m.204–9°;⁵⁵⁶ Et, m.202°.³⁵⁹
- 5,2-HS(NH₂)C₆H₅COOH, m.202°.³⁵⁹
- 2,4-HS(MeSO₂)C₆H₃COOH, m.181°.^{336.5}
- o*-HSeC₆H₄COOMe, b₃ 113–4°.³³⁷

BIBLIOGRAPHY

1. Emil Abderhalden and Ernst Wertheimer, *Arch. ges. Physiol.*, **197**, 131–46 (1922); **198**, 122–7 (1923); **199**, 336–51 (1923); **200**, 649–54 (1923)—*C.A.* **17**, 1810, 2121; **18**, 845.
2. E. P. Abraham, W. Baker, W. R. Boon, C. T. Calam, H. C. Carrington, E. Chain, H. W. Florey, G. G. Freeman, R. Robinson, and A. G. Sanders, *Chem. of Penicillin* (H. T. Clarke et al.) 1949, 10–37—*C.A.* **45**, 6185.
3. E. P. Abraham, E. Chain, W. Baker, and R. Robinson, *Nature*, **151**, 107 (1943)—*C.A.* **37**, 2346.

4. Aaron Addleston, *Chem. Industries*, 58, 414–15, 423 (1946)—*C.A.* 40, 2588.
- 4.5 A. Affonso and M. L. Khorana, *Indian J. Pharm.*, 12, 66–7 (1950)—*C.A.* 44, 7490.
5. Alfred Ahlqvist, *J. prakt. Chem.*, [2] 99, 45–84 (1919)—*C.A.* 14, 46–8.
6. Shiro Akabori, *J. Chem. Soc. Japan*, 52, 844–50 (1931); *Ber.*, 66, 151–8 (1933)—*C.A.* 26, 5076; 27, 1882.
7. W. J. Allan and F. E. Beamish, *Anal. Chem.*, 24, 1608–12 (1952)—*C.A.* 47, 68.
8. C. F. H. Allen and D. D. MacKay, *Org. Syntheses*, 12, 60–1 (1932)—*C.A.* 26, 3497.
9. C. E. Alm and F. E. Brauns, *J. Am. Chem. Soc.*, 61, 277–80 (1939)—*C.A.* 33, 2705.
10. American Cyanamid Co., (a) *Brit. pat.* 609,722 (1948); (b) 615,628 (1949)—*C.A.* 43, 1796, 4687.
11. Rudolf Andreasch, (a) *Ber.*, 12, 1385–90, 1390–2 (1879); (b) *ibid.*, 13, 1421–3 (1880); (c) *Monatsh.*, 16, 789–97 (1895); (d) *ibid.*, 18, 56–94 (1897); (e) *ibid.*, 38, 203–9 (1917)—*C.A.* 12, 1295.
12. J. C. Andrews, *J. Biol. Chem.*, 69, 209–17 (1926)—*C.A.* 20, 3158.
13. L. Anigstein, *Ann. maladies veneriennes*, 32, 544 (1937); *Ann. dermatol. syphil.*, 8, 963—*C.A.* 32, 3024.
14. Gladys A. Anslow and Mary Louise Foster, *J. Biol. Chem.*, 97, 37–46 (1932)—*C.A.* 26, 4752.
15. M. L. Anson, *J. Gen. Physiol.*, 25, 355–67 (1942)—*C.A.* 36, 4530.
16. Fritz Arndt and Nadji Bekir, *Ber.*, 63, 2390–3 (1930)—*C.A.* 25, 914.
17. J. N. Ashley and C. R. Harington, *J. Chem. Soc.*, 1930, 2586–90—*C.A.* 25, 1247.
18. Gunnar Axberg and Bror Holmberg, *Ber.*, 66, 1193–8 (1933)—*C.A.* 27, 5996.
19. W. E. Bachmann and M. W. Cronyn, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 849–891.
- 19.5. Badische Anilin- & Soda-Fabrik (Kurt Heintz), *Ger. pat.* 859,456 (1952)—*C.A.* 47, 11233.
20. Badische Anilin- u. Soda-Fabrik (Heinrich Kobbe), *Ger. pat.* 801,737 (1951)—*C.A.* 45, 3616.
21. Badische Anilin- u. Soda-Fabrik (Arnold Tartter), *Ger. pat.* 803,356 (1951)—*C.A.* 45, 8033.

22. Birger Bäcklund, *Arkiv. Kemi, Mineral. Geol.*, **14A** No. 1, 25 p. (1940)—C.A. **34**, 7860.
23. B. Bailey, Samuel Belfer, Howard Eder, and H. C. Bradley, *J. Biol. Chem.*, **143**, 721–8 (1942)—C.A. **36**, 4835.
24. J. L. Bailey, W. Bradley and The British Drug Houses Ltd., *Brit. pat.* 584,774 (1947)—C.A. **41**, 4509.
25. B. R. Baker, M. V. Querry, Seymour Bernstein, S. R. Safir, and Y. Subbarow, *J. Org. Chem.*, **12**, 167–73 (1947)—C.A. **41**, 2727.
26. B. R. Baker, M. V. Querry, S. R. Safir, and Seymour Bernstein, *J. Org. Chem.*, **12**, 138–54 (1947)—C.A. **41**, 2722.
27. Wilson Baker and P. G. Jones, *J. Chem. Soc.*, **1951**, 1143–5—C.A. **46**, 2050.
28. Wilson Baker and W. D. Ollis, *J. Chem. Soc.*, **1949**, 345–9; **1951**, 556–61—C.A. **43**, 7427; **45**, 9038.
29. H. J. Barber, (a) *J. Chem. Soc.*, **1929**, 1020–4, 1024–6; (b) *ibid.*, 2333–7; (c) *ibid.*, **1932**, 1365–9—C.A. **23**, 3677; **24**, 601; **26**, 4037.
30. H. J. Barber and May & Baker, Ltd., *Brit. pat.* 331,869 (1929)—C.A. **25**, 116.
31. G. Barger and F. P. Coyne, *Arch. sci. biol. (Italy)*, **12**, 141–4 (1928)—C.A. **23**, 170.
32. G. Barger and A. J. Ewins, *J. Chem. Soc.*, **99**, 2336 (1911)—C.A. **6**, 1154.
33. H. K. Barrenscheen and Hela Beneschovsky, *Biochem. Z.*, **255**, 453–63 (1932)—C.A. **27**, 743.
34. E. S. G. Barron and G. Kalinsky, *Biochem. J.*, **41**, 346–51 (1947)—C.A. **42**, 3003.
35. Hugo Bauer and Kurt Burschkies, *Ber.*, **66**, 1041–6 (1933)—C.A. **27**, 5059.
36. K. H. Bauer and J. Stockhausen, *J. prakt. Chem.*, [2] **130**, 35–44 (1931)—C.A. **25**, 3314.
37. E. Baumann, *Z. physiol. Chem.*, **8**, 299 (1884); *Ber.*, **18**, 258–67 (1886).
38. Emil Baur and H. Preis, *Z. physik. Chem.*, **B32**, 65–83 (1936)—C.A. **30**, 4387.
39. H. Beckurts and G. Frerichs, (a) *J. prakt. Chem.*, [2] **66**, 172–93 (1902); *ibid.*, **74**, 38–50 (1906); (b) *Arch. Pharm.*, **253**, 136–55, 155–81 (1915)—C.A. **10**, 47, 1519.
40. Otto Behagel and Martin Rollmann, *Ber.*, **62**, 2696–9 (1929)—C.A. **24**, 1344.
41. Otto Behagel and Ernst Schneider, *Ber.*, **68**, 1588–93 (1935)—C.A. **29**, 7960.

42. Jeanette A. Behre, *Biochem. J.*, **26**, 458-60 (1932)—C.A. **26**, 4352.
43. Jeanette A. Behre and S. R. Benedict, *J. Biol. Chem.*, **82**, 11-5 (1929)—C.A. **23**, 2733.
44. O. K. Behrens, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 657-679.
45. O. K. Behrens, Joseph Corse, R. G. Jones, Marjorie J. Mann, Q. F. Soper, F. R. Van Abeele, and Ming-Chien Chiang, *J. Biol. Chem.*, **175**, 751-64 (1948)—C.A. **43**, 2270.
46. Hans Behringer, *Ber.*, **81**, 326-7 (1948)—C.A. **43**, 4224.
47. Erich Benary, *Ber.*, **46**, 2103-7 (1913)—C.A. **7**, 3324.
48. S. R. Benedict, *J. Biol. Chem.*, **64**, 215-9 (1925)—C.A. **19**, 2351.
49. S. R. Benedict and Eleanor B. Newton, *J. Biol. Chem.*, **83**, 357-60, 361-5 (1929)—C.A. **23**, 5480.
50. S. R. Benedict, Eleanor B. Newton, and Jeanette A. Behre, *J. Biol. Chem.*, **67**, 267-77 (1926)—C.A. **20**, 1814.
51. R. Bentley, A. H. Cook, and J. A. Elvidge, (a) *J. Chem. Soc.*, 1949, 2357-62; (b) *ibid.*, 3216-20—C.A. **44**, 1487, 4900.
52. R. Bentley, A. H. Cook, J. A. Elvidge, and G. Shaw, *J. Chem. Soc.*, 1949, 2351-7—C.A. **44**, 1485.
53. C. J. Berg, E. A. Kaczka, and Karl Folkers to Merck & Co., Inc., *Brit. pat.* 621,915 (1949)—C.A. **44**, 667.
54. G. A. Berg and Bror Holmberg, *Svensk Kem. Tid.*, **47**, 257-65 (1935)—C.A. **30**, 2370.
55. Richard Berg and E. S. Fahrenkamp, *Z. anal. Chem.*, **112**, 161-9 (1938)—C.A. **32**, 4460.
56. Richard Berg, E. S. Fahrenkamp, and W. Roebeling, *Mikrochemie, Festschr. von Hans Molisch*, 1936, 42-51—C.A. **31**, 4234.
57. Richard Berg and W. Roebeling, *Ber.*, **68**, 403-7 (1935); *Angew. Chem.*, **48**, 430-2, 597-601 (1935)—C.A. **29**, 3330, 6525, 7885.
58. Max Bergmann and G. Michalis, *Ber.*, **63**, 98-9 (1930)—C.A. **24**, 3757.
59. Frederick Bernheim and Mary L. C. Bernheim, *Cold Springs Harbor Symposia Quant. Biol.*, **7**, 174-83 (1939)—C.A. **38**, 386.
60. Allan Bernton, *Dissertation, Uppsala*, 1932, 119 p.—C.A. **29**, 1429.
61. Theodor Bersin and Heinrich Köster, *Z. physiol. Chem.*, **233**, 59-66 (1935)—C.A. **29**, 4384.

62. Theodor Bersin and W. Logemann, *Ann.*, 505, 1-16 (1933)—*C.A.* 27, 5307.
63. Theodor Bersin and Juliane Steudel, *Ber.*, 71, 1015-24 (1938)—*C.A.* 32, 5283.
64. R. J. Best, *Australian J. Exptl. Biol. Med. Sci.*, 17, 1-17 (1939)—*C.A.* 33, 5887.
65. C. F. Bickford and R. E. Schoetzow, *J. Am. Pharm. Assoc.*, 26, 409-11 (1937)—*C.A.* 31, 5107.
66. Einar Biilmann, (a) *Ann.*, 339, 351-72 (1905); (b) *ibid.*, 348, 120-43 (1906); (c) *ibid.*, 364, 314-29 (1909)—*C.A.* 3, 1521.
67. Einar Biilmann and E. H. Madsen, *Ann.*, 402, 331-42 (1914)—*C.A.* 8, 1101.
68. J. D. Billimoria, A. H. Cook, and Ian Heilbron, *J. Chem. Soc.*, 1949, 1437-40—*C.A.* 44, 1964.
69. Léon Binet and E. Robillard, *Compt. rend. soc. biol.*, 129, 533-4 (1938)—*C.A.* 33, 999.
70. Léon Binet, Georges Weller, and Eugène Robillard, *Compt. rend. soc. biol.*, 131, 954-6 (1939)—*C.A.* 33, 8796.
71. Jannik Bjerrum, *J. Biol. Chem.*, 114, 357-9 (1936)—*C.A.* 30, 5525.
72. Konrad Bloch and H. T. Clarke, *J. Biol. Chem.*, 125, 275-87 (1938)—*C.A.* 32, 9040.
73. W. D. Block, O. H. Buchanan, and R. H. Freyberg, *J. Pharmacol.*, 73, 200-4 (1941); *ibid.*, 76, 355-7 (1942); *ibid.*, 82, 391-8 (1944)—*C.A.* 36, 565; 37, 1194; 39, 1687.
74. Doris Blumenthal, *J. Biol. Chem.*, 113, 433-7 (1936)—*C.A.* 30, 3876.
- 74.5. Julius Böss, *Seifen-Öle-Fette-Wachse*, 79, 107-8 (1953)—*C.A.* 47, 7738.
75. Carl Böttinger, (a) *Ber.*, 11, 1352-3 (1878); (b) *ibid.*, 9, 404-5, 802-4, 1061-4 (1876); *ibid.*, 18, 486 (1885); *Ann.*, 188, 293-342 (1877); (c) *ibid.*, 196, 92-108 (1879); (d) *ibid.*, 198, 203-28 (1879).
76. Karel Bohemen, *Brit. pat.* 484,467 (1938)—*C.A.* 32, 8082.
77. J. Bongartz, *Ber.*, 19, 1931-5 (1886); *ibid.*, 21, 478-87 (1888).
78. Henry Borsook, E. L. Ellis, and H. M. Huffman, *J. Biol. Chem.*, 117, 281-308 (1937)—*C.A.* 31, 2917.
79. Joseph Bougault, Eugène Cattelain, and Pierre Chabrier, *Compt. rend.*, 208, 657-9 (1939); *Bull. soc. chim.*, [5], 7, 781-9 (1940)—*C.A.* 33, 4580; 36, 2198.

80. D. Bramley and N. H. Chamberlain, *J. Chem. Soc.*, 1942, 376—C.A. 36, 5156.
81. Erwin Brand, R. J. Block, and G. F. Cahill, *J. Biol. Chem.*, 119, 689–96 (1937)—C.A. 31, 7520.
82. Erwin Brand, G. F. Cahill, and R. J. Block, *J. Biol. Chem.*, 110, 399–410 (1935)—C.A. 29, 5499.
83. Julius von Braun, *Ber.*, 35, 3368–88 (1902).
84. F. E. Brauns and M. A. Buchanan, *Paper Trade J.*, 122, No. 21, 49–58 (1946)—C.A. 40, 5245.
85. R. Brdicka, (a) *Coll. Czech. Chem. Com.*, 5, 148–64 (1933); (b) *Biochem. Z.*, 272, 104–12 (1934)—C.A. 28, 7131.
86. J. H. Brewer, *J. Bact.*, 39, 10 (1940)—C.A. 34, 2017.
87. The British Drug Houses Ltd., Wm. Bradley, and Michael Davis, *Brit. pat.* 586,004 (1947)—C.A. 42, 211.
88. E. V. Brown, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 473–534—C.A. 44, 146.
89. R. Brown, W. E. Jones, and A. R. Pinder, *J. Chem. Soc.*, 1951, 2123–5—C.A. 46, 2486.
90. G. Brownlee and Malcolm Woodbine, *Brit. J. Pharmacol.*, 3, 305–8 (1948)—C.A. 43, 2737.
91. Alexander Brunschwig, Charles Johnson, and Sabra Nichols, *Proc. Soc. Exptl. Biol. Med.*, 60, 388–91 (1945)—C.A. 40, 1935.
92. Felice Bucci, *Ann. chim.*, 42, 193–204 (1952)—C.A. 46, 9472.
93. W. J. Burke to DuPont Co., *U.S. pat.* 2,388,597 (1945)—C.A. 40, 1033.
94. W. J. Burke and F. T. Peters to Canadian Industries, Ltd., *Can. pat.* 428,507 (1945)—C.A. 39, 5254.
95. W. J. Burke and F. T. Peters to DuPont Co., *U.S. pat.* 2,268,185 (1941)—C.A. 36, 2569.
96. F. Buscaróns and J. Artigas, *Anales real soc. españ. fis. y quim.*, 48B, 140–2 (1952), 49B, 375–8, 379–86 (1953)—C.A. 46, 10044; 48, 2524.
- 96.5. F. Buscaróns, J. Artigas, and F. Capitan, *Anales real soc. españ. fis. y quim.* (Madrid), 47B, 131–4 (1951); *ibid.*, 48B, 183 (1952)—C.A. 45, 7963; 47, 4302.
97. F. Buscaróns and F. Capitan, *Anales real soc. españ. fis. y quim.*, 46B 453–62, 569–76 (1950)—C.A. 45, 5073.
98. Adolf Butenandt, Horst Jalzkewitz, and Paul Fouché, *Z. physiol. Chem.*, 282, 268–71 (1947)—C.A. 43, 5742.

99. Adolf Butenandt, Horst Jatzkewitz, and Ulrich Schiedt, *Z. physiol. Chem.*, **285**, 238–43 (1950)—C.A. **45**, 5624.
100. Ng. Ph. Buu-Hoi and Paul Cagniant, *Ber.*, **75**, 1181–9 (1942)—C.A. **37**, 4706.
101. R. K. Cannan and B. C. J. G. Knight, *Biochem. J.*, **21**, 1384–90 (1927)—C.A. **22**, 1083.
102. N. O. Cappel and Leona R. Cappel, *Am. Perfumer*, **48**, No. 8, 43–5 (1946)—C.A. **40**, 6667.
103. H. M. E. Cardwell, *J. Chem. Soc.*, **1949**, 715–19—C.A. **43**, 7433.
104. L. Carius, (a) *Ann.*, **124**, 43–57 (1862); (b) *ibid.*, **129**, 6–14 (1864).
105. G. Carpeni and Pierre Souchay, *Brit. pat.* 624,568 (1949)—C.A. **44**, 4026.
106. F. H. Carpenter, G. W. Stacy, Dorothy S. Genghof, A. H. Livermore, and Vincent du Vigneaud, *J. Biol. Chem.*, **176**, 915–27 (1948)—C.A. **43**, 1768.
107. F. H. Carpenter, R. A. Turner, and Vincent du Vigneaud, *J. Biol. Chem.*, **176**, 893–906 (1948)—C.A. **43**, 1768.
108. H. E. Carter, C. M. Stevens, and L. F. Ney, *J. Biol. Chem.*, **139**, 247–54 (1941)—C.A. **35**, 5463.
109. J. R. Catch, A. H. Cook, A. R. Graham, and Ian Heilbron, *Nature*, **159**, 578–9 (1947); *J. Chem. Soc.*, **1947**, 1609–13—C.A. **41**, 4774; **42**, 2931.
110. C. J. Cavallito and T. H. Haskell, *J. Am. Chem. Soc.*, **67**, 1991–4 (1945)—C.A. **40**, 837.
111. Paulette Chaix and Claude Fromageot, *Compt. rend.*, **202**, 983–4 (1936); *Enzymologia*, **1**, 321–7 (1937)—C.A. **30**, 4527; **31**, 5006.
112. G. C. Chattuck and P. T. Willis, *J. Trop. Med.*, **31**, 115–6 (1928)—C.A. **22**, 4648.
113. Chem. Fab. Flora, *Brit. pat.* 156,103 (1920)—C.A. **15**, 1782.
114. Chem. Fabrik von Heyden A.-G. (Kurt Buchheim), *Ger. pat.* 514,507 (1928)—C.A. **25**, 2155.
- 114.5. Chemische Werke Hüls (Wilhelm Dietrich and Heinrich Weber), *Ger. pat.* 859,457 (1952)—C.A. **48**, 2088.
115. Graham Chen, E. M. K. Geiling, and R. M. MacHatton, *J. Infectious Diseases*, **76**, 144–51, 152–4 (1945)—C.A. **39**, 4973.
116. E. M. Chenery, *Analyst*, **73**, 501–2 (1948)—C.A. **43**, 2889.
117. L. C. Cheney and J. R. Piening, *J. Am. Chem. Soc.*, **67**, 731–5 (1945)—C.A. **39**, 3280.

118. E. Cherbuliez and P. Plattner, *Helv. chim. acta*, **12**, 317–29 (1929)—C.A. **23**, 5161.
119. W. G. Christiansen and W. M. Lauter to E. R. Squibb and Sons, U.S. pat. 1,859,288 (1932)—C.A. **26**, 3877.
- 119.5. I. P. P. Christophe, *Fr. pat.* 896,443 (1945)—C.A. **47**, 11246.
120. R. E. D. Clark, *J. Chem. Soc.*, **1932**, 1826–30—C.A. **26**, 4332.
121. H. T. Clarke and J. M. Inouye, *J. Biol. Chem.*, **89**, 399–419 (1930)—C.A. **25**, 685.
122. H. T. Clarke, J. R. Johnson, and Robert Robinson, editors, *The Chemistry of Penicillin*, Princeton University Press, 1949.
123. H. T. Clarke, J. R. Johnson, and Robert Robinson, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 3–9.
124. A. Claus, *Ann.*, **179**, 145–8 (1875).
125. Erik Clemmensen and A. H. C. Heitman, *Am. Chem. J.*, **40**, 280–302 (1908)—C.A. **2**, 3227.
126. Archibald Clow and J. M. C. Thompson, *Trans. Faraday Soc.*, **33**, 894–904 (1937)—C.A. **31**, 6941.
127. Aaron Cohen, *J. Chem. Soc.*, **1932**, 593–8—C.A. **26**, 2438.
128. Aaron Cohen, Harold King, and W. I. Strangeways, *J. Chem. Soc.*, **1931**, 3043–57—C.A. **26**, 1262.
129. S. J. Cohen, *J. Pharmacol.*, **35**, 343–50 (1929)—C.A. **23**, 3982.
130. F. E. Condo, E. T. Hinkel, A. Fassero, and R. L. Shriner, *J. Am. Chem. Soc.*, **59**, 230–2 (1937)—C.A. **31**, 1762.
131. A. H. Cook, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 106–43.
132. A. H. Cook and J. A. Elvidge, *J. Chem. Soc.*, **1949**, 2362–7—C.A. **44**, 1488.
133. A. H. Cook, J. A. Elvidge, and G. Shaw, *J. Chem. Soc.*, **1949**, 2367–70—C.A. **44**, 1489.
134. A. H. Cook, G. Harris, J. R. A. Pollock, and J. M. Swan, *J. Chem. Soc.*, **1950**, 1947–54—C.A. **45**, 1999.
135. A. H. Cook and I. M. Heilbron, (a) *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 38–51; (b) *ibid.*, 921–72—C.A. **45**, 6186; **44**, 9427.
136. E. W. Cook and Samuel Kushner to Am. Cyanamid Co., U.S. pat. 2,494,745 (1950)—C.A. **44**, 5395.
137. E. W. Cook, Samuel Kushner, and P. H. Moss to Am. Cyanamid Co., U.S. pat. 2,552,478 (1951)—C.A. **46**, 144.

138. R. J. Coons and C. A. Todaro to Gillette Safety Razor Co., U.S. pat. 2,594,030 (1952)—C.A. 47, 2200.
139. F. C. Copp and Samuel Wilkinson to Wellcome Foundation Ltd., Brit. pat. 596,547 (1948)—C.A. 42, 5472.
140. J. W. Cornforth, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 688–848.
141. J. W. Cornforth, E. Fawaz, L. J. Goldsworthy, and Robert Robinson, *J. Chem. Soc.*, 1949, 1549–53—C.A. 44, 549.
142. J. W. Cornforth and H. T. Huang, *J. Chem. Soc.*, 1948, 1964–9—C.A. 43, 2989.
143. J. W. Corse, R. G. Jones, Q. F. Soper, C. W. Whitehead, and O. K. Behrens, *J. Am. Chem. Soc.*, 70, 2837–43 (1948)—C.A. 43, 3360.
144. Joseph W. Corse, E. C. Kleiderer, and Q. F. Soper, *J. Am. Chem. Soc.*, 70, 438–9 (1948)—C.A. 42, 2234.
145. Ruth Cortell and R. K. Richards, *Proc. Soc. Exptl. Biol. Med.*, 49, 121–3 (1942)—C.A. 36, 2624.
146. L. H. Cotter, *J. Am. Med. Assoc.*, 131, 592–3 (1946)—C.A. 40, 4802.
147. P. P. Coustolle, *Fr. pat.* 46,213 (1936)—C.A. 30, 7284.
148. H. M. Crooks, Jr., *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 455–72—C.A. 44, 9435.
149. H. M. Crooks, Jr., to Parke, Davis & Co., U.S. pat. 2,430,455 (1947)—C.A. 42, 1317.
150. D. Crowfoot, C. W. Bunn, B. W. Rogers-Low, and A. Turner-Jones, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 310–66—C.A. 43, 4919.
151. E. G. Curphey, *Chemistry & Industry*, 1951, 840–1—C.A. 46, 7523.
- 151.5. J. F. Danielli, Mary Danielli, J. B. Fraser, P. D. Mitchell, L. N. Owen, and G. Shaw, *Biochem. J.*, 41, 325–8 (1947)—C.A. 42, 3859.
152. M. H. Dawson and G. L. Hobby, *J. Pharmacol.*, 69, 359–64 (1940)—C.A. 34, 6706.
153. A. W. K. de Jong, *Rec. trav. chim.*, 21, 295–8 (1902).
154. Raymond Delaby and Jean Hubert, *Bull. soc. chim.*, [5] 10, 576–80 (1943)—C.A. 38, 4562.
155. Raymond Delange to Fabriques des produits de chimie organique de Laire, U.S. pat. 2,049,198 (1936)—C.A. 30, 6514.
156. Marcel Delépine to Soc. des usines chim. Rhone-Poulenc, U.S. pat. 1,994,213 (1935)—C.A. 29, 3121.

157. Marcel Delépine and Paul Gailliot to Soc. des usines chim. Rhône-Poulenc, U.S. pat. 2,060,181 (1936)—C.A. 31, 507.
158. Gaetano Del Vecchio and Roberto Argenziano, *Boll. soc. ital. biol. sper.*, 22, 1189-90 (1946)—C.A. 41, 6297.
159. Gaetano Del Vecchio, Vittorio Del Vecchio, and Roberto Argenziano, *Boll. soc. ital. biol. sper.*, 23, 451-3, 1023-5 (1947)—C.A. 42, 1624, 6401.
160. C. W. Denko and A. K. Anderson, (a) *J. Lab. Clin. Med.*, 29, 1168-76 (1944); (b) *J. Am. Chem. Soc.*, 67, 2241 (1945)—C.A. 39, 4383; 40, 1542.
161. F. DeRitis and L. Scalfi, *Boll. soc. ital. biol. sper.*, 20, 852-4 (1945)—C.A. 40, 6544.
162. Deutsche Hydrierwerke (Richard Hueter), *Ger. pat.* 648,-936 (1933)—C.A. 31, 8548.
163. A. N. Dey, *J. Chem. Soc.*, 1937, 1166-8—C.A. 31, 7058.
164. Malcolm Dixon and Juda H. Quastel, *J. Chem. Soc.*, 123, 2943-53 (1923)—C.A. 18, 380.
165. Malcolm Dixon and H. E. Tunnicliffe, *Proc. Roy. Soc. London*, 94B, 266-97 (1923)—C.A. 17, 3016.
166. J. J. Donleavy, Jr., and James English, Jr., *J. Am. Chem. Soc.*, 62, 220-1 (1940)—C.A. 34, 1640.
167. Richard Donovan and Geoffrey Rake, *Proc. Soc. Exptl. Biol. Med.*, 61, 224-7 (1946)—C.A. 40, 4103.
168. B. B. Drake, C. V. Smythe, and C. G. King, *J. Biol. Chem.*, 143, 89-98 (1942)—C.A. 36, 3786.
- 168.5. J. J. Draney, Jr., and Michael Cefola, *J. Am. Chem. Soc.*, 76, 1975-7 (1954)—C.A. 48, 8628.
169. H. Dreyfus to Celanese Corp. of America, U.S. pat. 2,316,-847 (1943)—C.A. 37, 5736.
170. A. M. Drummond and D. T. Gibson, *J. Chem. Soc.*, 1926, 3073-7—C.A. 21, 908.
171. J. V. Dubsky, *Microchemie*, 28, 145-72 (1940)—C.A. 34, 4686.
172. J. V. Dubsky and B. Mareth, *Microchemie ver Mikrochim. Acta*, 29, 213-18 (1941)—C.A. 37, 4320.
173. J. V. Dubsky and V. Sindelar, (a) *Mikrochim. Acta*, 3, 258-62 (1938); (b) *Mikrochemie*, 24, 264-7 (1938)—C.A. 32, 6077, 7855.
174. W. M. Duffin and Samuel Wilkinson to Therapeutic Research Corp. of Great Britain Ltd., U.S. pat. 2,450,784 (1948)—C.A. 44, 286.
175. W. M. Duffin and Samuel Wilkinson to Wellcome Foundation Ltd., *Brit. pat.* 585,436 (1947)—C.A. 41, 4175.

176. E. I. du Pont de Nemours & Co., (a) Fr. pat. 821,580 (1937); (b) Brit. pat. 592,631 (1947)—C.A. 32, 3766; 42, 2277.
177. J. D. Dutcher, J. R. Johnson, and W. F. Bruce, J. Am. Chem. Soc. 67, 1736-45 (1945)—C.A. 40, 81.
178. E. Duvillier, Compt. rend., 86, 47 (1878)—Bull. soc. chim., [2] 30, 506-7 (1878).
179. G. M. Dyson, Pharm. J., 123, 431 (1929)—C.A. 24, 2546.
180. Harry Eagle, J. Pharmacol., 66, 436-48 (1939)—C.A. 33, 7888.
181. Harry Eagle, F. G. Germuth, Jr., H. J. Magnuson, Ralph Fleischman, Jean C. Grossberg, and Claire E. Tucker, J. Pharmacol., 89, 196-204 (1947)—C.A. 41, 3210.
182. B. A. Eagles, J. Am. Chem. Soc., 50, 1386-7 (1928)—C.A. 22, 2142.
183. B. A. Eagles and T. B. Johnson, J. Am. Chem. Soc., 49, 575-80 (1927)—C.A. 21, 915.
184. E. Eberius, Angew. Chem., 63, 513-9 (1951)—C.A. 46, 854.
185. Alfred Eckert and Ottokar Halla, Monatsh., 34, 1811-3 (1913)—C.A. 8, 500.
186. A. H. Eggerth, J. Exptl. Med., 53, 27-36 (1931)—C.A. 25, 982.
187. I. Z. Eiger and J. P. Greenstein, Arch. Biochem., 19, 467-73 (1948)—C.A. 45, 8978.
188. J. Eisenbrand and F. Wegel, Z. physiol. Chem., 268, 26-49 (1941)—C.A. 36, 2494.
- 188.5. D. F. Elliott and Charles Harington, J. Chem. Soc., 1949, 1374-8—C.A. 44, 571.
189. K. A. C. Elliott, Biochem. J., 24, 310-26 (1930)—C.A. 24, 5584.
190. H. Elöd, H. Nowotny, and H. Zahn, Kolloid-Z., 100, 283-98 (1942)—C.A. 37, 3611.
191. Emil Erlenmeyer, Jr., Ber., 36, 2720-2 (1903).
192. Emil Erlenmeyer, Jr., and F. Stoop, Ann., 337, 259-63 (1904).
193. Etab. Poulenc frères and Carl Oechslin, Fr. pat. 643,911 (1927)—C.A. 23, 1649.
194. Hans v. Euler and John Hagen, Z. phys. Chem., A 171, 379-84 (1934)—C.A. 29, 2826.
195. R. L. Evans, Brit. pat. 670,702 (1952)—C.A. 47, 2201.
196. R. L. Evans and E. G. McDonough, Fr. pat. 844,529 (1939)—C.A. 34, 7658.

197. R. L. Evans and E. G. McDonough to Sales Affiliates, Inc., U.S. pat. 2,352,524 (1944)—C.A. 38, 5646.
198. R. M. Evans and L. N. Owen, *J. Chem. Soc.*, 1949, 244—8—C.A. 43, 7423.
199. W. L. Evers to Socony-Vacuum Oil Co., U.S. pat. 2,088,193 (1937)—C.A. 31, 6867.
200. Farbwk. vorm Meister Lucius & Brüning, (a) Ger. pat. 203,882, 211,679 (1906); (b) Brit. pat. 157,226 (1921)—C.A. 3, 724, 2491; 15, 1965.
201. M. W. Farlow, *J. Biol. Chem.*, 176, 71–2 (1948)—C.A. 43, 2166.
202. M. W. Farlow to Du Pont Co., U.S. pat. 2,406,362 (1946)—C.A. 40, 7233.
203. M. W. Farlow, W. A. Lazier, and F. K. Signaigo, *Ind. Eng. Chem.*, 42, 2547–9 (1950)—C.A. 45, 2852.
204. M. W. Farlow and F. K. Signaigo to Du Pont Co., (a) U.S. pat. 2,402,613 (1946); (b) 2,402,615 (1946)—C.A. 40, 5758, 5760.
205. Adolf Feldt, Walter Schoeller, and H. G. Allardt to Schering-Kahlbaum, U.S. pat. 2,036,208 (1936)—C.A. 30, 3593.
- 205.3. C. F. Ferraro, J. J. Draney, and Michael Cefola, *J. Am. Chem. Soc.*, 75, 1203–8 (1953)—C.A. 47, 5747.
- 205.5. Lamar Field and R. O. Beauchamp, Jr., *J. Am. Chem. Soc.*, 74, 4707–8 (1952)—C.A. 48, 6963.
206. L. F. Fieser and R. B. Turner, *J. Am. Chem. Soc.*, 69, 2335–8 (1947)—C.A. 42, 1250.
207. Emil Fischer and Walter Brieger, *Ber.*, 47, 2469–78 (1914)—C.A. 9, 77.
208. Emil Fischer and Karl Raske, *Ber.*, 41, 893–7 (1908).
209. E. K. Fischer, *J. Biol. Chem.*, 89, 753–63 (1930)—C.A. 25, 916.
210. H. J. Fisher, W. T. Mathis, and D. C. Walden, *Conn. Agr. Expt. Sta. (New Haven) Bull.*, 460, 448–50 (1942); 34th Rept. on Drug Products—C.A. 36, 7232.
211. L. Flatow, *Biochem. Z.*, 194, 132–9 (1928)—C.A. 22, 2763.
212. William Fletcher, *Fr. pat.* 824,804 (1938)—C.A. 32, 6404.
213. Zoltan Földi and Janos Kollonitsch, *J. Chem. Soc.*, 1948, 1683–5—C.A. 43, 1722.
214. A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.*, 1949, 1754–7—C.A. 44, 1439.
215. P. Fouche, *Fr. pat.* 957,225 (1950)—C.A. 46, 9586.
216. S. W. Fox and Milton Winitz, *Arch. Biochem. Biophys.*, 35, 419–27 (1952)—C.A. 46, 5637.

217. Sigmund Fränkel, *Monatsh.*, **24**, 231 (1903).
218. H. L. Fraenkel-Conrat, *J. Biol. Chem.*, **142**, 119–27 (1942)—*C.A.* **36**, 1998.
219. H. L. Fraenkel-Conrat, M. E. Simpson, and H. M. Evans, (a) *Science*, **91**, 363–5 (1940); (b) *J. Biol. Chem.*, **142**, 107–17 (1942)—*C.A.* **34**, 4444; **36**, 1997.
220. Hartwig Franzen, *Sitzb. Heidelberg Akad. Wiss. Math-naturw. Klasse*, **1910**, 54 pp.—*C.A.* **5**, 2665.
221. J. B. Fraser, L. N. Owen, and G. Shaw, *Biochem. J.*, **41**, 328–33 (1947)—*C.A.* **42**, 4128.
222. Arne Fredga, (a) *Ber.*, **71**, 289–95 (1928); *Arkiv. Kemi, Mineral. Geol.*, **14B**, No. 15, 5 p. (1940); (b) *ibid.*, **13A**, No. 5, 18 p. (1938); (c) *ibid.*, **15**, No. 23, 1–6 (1942)—*C.A.* **32**, 2906; **35**, 2115; **33**, 456; **37**, 5953.
223. Arne Fredga and Olle Martensson, *Arkiv. Kemi, Mineral. Geol.*, Ser. B, **16**, No. 8, 1–6 (1942)—*C.A.* **38**, 3616.
- 223.5. L. D. Freedman and A. H. Corwin, *J. Biol. Chem.*, **181**, 601–21 (1949)—*C.A.* **44**, 2577.
224. Karl Freudenberg, Martin Meister, and Erich Flickinger, *Ber.*, **70**, 500–14 (1937)—*C.A.* **31**, 3878–80.
225. R. H. Freyberg, *Proc. Staff Meetings Mayo Clinic*, **17**, 534–41 (1942)—*C.A.* **37**, 683.
226. R. H. Freyberg, W. D. Block, and S. Levey, *J. Clin Investigation*, **20**, 401–12 (1941)—*C.A.* **35**, 7535.
227. Julian Freydl, *Sitzber.*, **98**, 65–8 (1889); *Monatsh.*, **10**, 83–85 (1889).
228. Hans Freytag, (a) *Z. anal. Chem.*, **137**, 331–44 (1953); (b) *ibid.*, **139**, 263–7 (1953)—*C.A.* **47**, 3185, 12129.
229. E. Friedberger, *Berl. Klin. Wochschr.*, **45**, 1714–7 (1908)—*C.A.* **3**, 200.
230. E. A. H. Friedheim, *Brit. pat.* 655,435 (1951)—*C.A.* **47**, 144.
231. Paul Friedländer, *Ber.*, **39**, 1065–6 (1906).
232. Paul Friedländer and A. Chwala, *Monatsh.*, **28**, 247–80 (1907).
233. Ernst Friedmann, (a) *Beitr. Chem. Physiol. Path.*, **3**, 184–92 (1903); (b) *J. prakt. Chem.*, [2] **146**, 179–92 (1936)—*C.A.* **30**, 8158.
234. Ernst Friedmann and Julius Baer, *Beitr. Chem. Physiol. Path.*, **8**, 326 (1906).
235. Ernst Friedmann and Joseph Girsavicius, *Biochem. J.*, **30**, 1886–91 (1936)—*C.A.* **31**, 1442.

236. K. Fries and H. Mengel, *Ber.*, **45**, 3408–11 (1912)—C.A. **7**, 2194.
237. Claude Fromageot and P. Desnuelle, *Compt. rend.*, **214**, 647–8 (1942)—C.A. **37**, 6281.
238. Claude Fromageot, Radwan Moubasher, and Pierre Desnuelle, *Enzymologia*, **2**, 344–9 (1938)—C.A. **33**, 6366.
239. Edouard Frommel, A. D. Herschberg, and Jeanne Piquet, *Compt. rend. soc. phys. hist. nat. Genève*, **60** (in *Arch. sci. phys. nat.*, **25**), 97–100 (1943)—C.A. **39**, 4898.
240. J. S. Fruton and H. T. Clarke, *J. Biol. Chem.*, **106**, 667–91 (1934)—C.A. **29**, 454.
241. S. Gabriel and J. Colman, *Ber.*, **41**, 513–21 (1907)—C.A. **2**, 1425.
242. Yvonne Garreau, *Compt. rend. soc. biol.*, **137**, 176–7 (1943); *ibid.*, **138**, 241–2 (1944)—C.A. **38**, 1835; **39**, 4644.
243. Ludwig Gattermann, *Ber.*, **32**, 1136–59 (1899).
244. Peter Gaubert to Imp. Chem. Ind. Ltd., *Brit. pat.* 591,435 (1947)—C.A. **42**, 592.
- 244.5. B. Gauthier and J. Maillard, *Ann. pharm. franc.*, **11**, 509–22 (1953)—C.A. **48**, 663.
245. J. R. Geigy A.-G., *Swiss pat.* 227,349 (1943)—C.A. **43**, 3039.
246. L. Genevois and P. Cayrol, *Bull. soc. chim.*, [5] **6**, 1223–30 (1939)—C.A. **33**, 8571.
247. J. C. Ghosh and S. C. Ganguli, *Biochem. J.*, **28**, 381–3 (1934)—C.A. **28**, 4651.
248. J. C. Ghosh and P. C. Rakshit, *Biochem. Z.*, **294**, 330–5 (1937)—C.A. **32**, 1726.
249. J. C. Ghosh, S. N. Raychaudhuri, and S. C. Ganguli, *J. Indian Chem. Soc.*, **9**, 43–52, 53–4 (1932)—C.A. **26**, 3976.
- 249.5. Gillette Safety Razor Co., *Brit. pat.* 695,493 (1953)—C.A. **47**, 10551.
250. Henry Gilman, C. E. Arntzen, and F. J. Webb, *J. Org. Chem.*, **10**, 374–9 (1945)—C.A. **40**, 325.
251. Henry Gilman and J. D. Robinson, *Rec. trav. chim.*, **49**, 766–8 (1930)—C.A. **24**, 4758.
252. Henry Gilman and H. L. Yale, *J. Am. Chem. Soc.*, **73**, 2880–1 (1951)—C.A. **46**, 3974.
253. J. Ginsberg and S. Bondzynski, *Ber.*, **19**, 114 (1886).
254. R. H. Glauert and F. G. Mann, *J. Chem. Soc.*, **1952**, 2127–35—C.A. **47**, 1125.
255. B. F. Goodrich Co., *Brit. pat.* 639,679 (1950)—C.A. **45**, 2971.

256. G. A. C. Gough and Harold King, *J. Chem. Soc.*, 1930, 673—C.A. 24, 3236.
- 256.5. E. H. Graul, *Dermatol. Wochschr.*, 121, 579–87 (1950)—C.A. 47, 9573.
257. John Green and Alexander Brunschwig, *Proc. Soc. Exptl. Biol. Med.*, 61, 348–50 (1946)—C.A. 40, 4120.
258. Jesse P. Greenstein, *J. Biol. Chem.*, 109, 529–40 (1935)—C.A. 29, 4749.
259. T. L. Gresham to B. F. Goodrich Co., U.S. pat. 2,449,989 (1948)—C.A. 43, 1054.
- 259.5. M. F. Gribbons, F. W. Miller, Jr., and D. K. O'Leary to Du Pont Co., U.S. pat. 2,397,960 (1946)—C.A. 40, 3542.
260. Gerhard Günther, *Pharmazie*, 5, 577–82 (1950)—C.A. 45, 7566.
261. J. M. Gulland and R. A. Peters, *Biochem. J.*, 24, 91–104 (1930)—C.A. 24, 5818.
262. K. D. Gundermann and Fritz Micheel, *Ann.*, 578, 45–8 (1952)—C.A. 47, 5353.
263. Martin Gunter and A. C. Ivy, *Proc. Soc. Exptl. Biol. Med.*, 70, 623–4 (1949)—C.A. 43, 5118.
264. Hans Hahl, (a) U.S. pat. 1,555,663 (1925); (b) 1,616,366 (1927)—C.A. 19, 3566; 21, 987.
265. Hans Hahl and H. Weyland, U.S. pat. 1,517,002 (1924)—C.A. 19, 380.
266. C. S. Hamilton to Parke, Davis and Co., U.S. pat. 2,331,833 (1943)—C.A. 38, 1609.
267. F. S. Hammett, *Proc. Am. Phil. Soc.*, 68, 151–61 (1929)—C.A. 23, 5225.
268. C. A. Handley and Marguerite La Forge, *Proc. Soc. Exptl. Biol. Med.*, 65, 74–5 (1947)—C.A. 41, 5626.
269. W. C. Harden and Fitzgerald Dunning, *J. Am. Chem. Soc.*, 49, 1017–8 (1927)—C.A. 21, 1631.
270. C. R. Harington and Johan Overhoff, *Biochem. J.*, 27, 338–44 (1933)—C.A. 27, 3711.
271. L. J. Harris, *Biochem. J.*, 16, 739–46 (1922)—C.A. 17, 775.
272. D. C. Harrison, (a) *Biochem. J.*, 18, 1009–22 (1924); (b) *ibid.*, 21, 1404–5 (1927)—C.A. 19, 430; 22, 1086.
273. L. E. Hart, E. W. McClelland, and F. S. Fowkes, *J. Chem. Soc.*, 1938, 2114–17—C.A. 33, 1726.
274. E. F. Hartung and Joyce Cotter, *J. Lab. Clin. Med.*, 26, 1274–84 (1941)—C.A. 35, 4494.
275. E. F. Hartung, Joyce Cotter, and Catherine Gannon, *J. Lab. Clin. Med.*, 26, 1750–5 (1941)—C.A. 35, 7031.

- 275.5. R. S. Hawley to S. O. Dev. Co., U.S. pat. 2,632,735 (1953)—C.A. 47, 6647.
276. H. Heath, Alexander Lawson, and C. Rimington, *Nature*, 166, 106 (1950); *J. Chem. Soc.*, 1951, 2215-7, 2217-20, 2220-2, 2223-5—C.A. 45, 2478; 46, 974.
277. J. Hebling, *Biochem. Z.*, 28, 208-12 (1910)—C.A. 5, 523.
278. I. M. Heilbron and A. H. Cook to Therapeutic Research Corp. of Great Britain Ltd., Brit. pat. 595,958 (1947)—C.A. 42, 3781.
279. I. M. Heilbron, A. H. Cook, and J. R. Catch, Brit. pat. 607,539 (1948)—C.A. 43, 4688.
280. F. R. Heilman, *Science*, 91, 366-7 (1940)—C.A. 34, 4462.
281. W. Heintz, *Ann.*, 136, 223-49 (1865).
282. Nils Hellström, (a) *Z. physik. Chem.*, A157, 242-68 (1931); *ibid.*, A163, 33-52 (1932); *ibid.*, A169, 416-24 (1934); *Arkiv Kemi, Min. Geol.*, 13A, No. 6, 1-7 (1938); (b) *Svensk Kem. Tid.*, 45, 157-69 (1933)—C.A. 26, 965; 27, 1617; 29, 119; 33, 3334; 28, 73.
283. Nils Hellström and Tore Lauritzon, (a) *Ber.* 69, 1999-2003 (1936); (b) *ibid.*, 2003-6—C.A. 30, 6707.
284. Nils Hellström and Bengt Lindberg, *Svensk Kem. Tid.*, 56, 181-93 (1944)—C.A. 40, 3724.
285. Henkel & Cie., Brit. pat. 470,717 (1937); *Ger. pat.* 684,239 (1939)—C.A. 32, 593; 34, 3283.
286. W. C. Hess and M. X. Sullivan, *J. Biol. Chem.*, 121, 323-9 (1937)—C.A. 32, 496.
287. A. J. Hijman and A. G. van Veen, *Geneeskund. Tijdschr. Nederland. Indie*, 76, 840-59 (1936)—C.A. 30, 4880.
288. R. M. Hill and H. B. Lewis, *J. Biol. Chem.*, 59, 557-67 (1924)—C.A. 18, 2189.
289. O. Hinsberg, *Ber.*, 43, 651-4 (1910)—C.A. 4, 1307.
290. Erwin Hoffa and Hans Heyna to General Aniline, U.S. pat. 1,762,270 (1913)—C.A. 24, 3800.
291. M. J. Hogue, *Am. J. Trop. Med.*, 14, 443-56 (1934)—C.A. 29, 2231.
292. E. R. Holiday, *Biochem. J.*, 24, 619-25 (1930)—C.A. 24, 4795.
293. Bror Holmberg, (a) *Ann.*, 353, 131-8 (1907); (b) *Ber.*, 65, 1348-9; (1932) (c) *ibid.*, 1349-54; *Rubber Chem. Tech.*, 6, 71-5 (1933); (d) *Ber.*, 69, 115-9 (1936); (e) *ibid.*, 75, 1760-4 (1942)—C.A. 1, 2233; 26, 5927, 6180; 27, 6014; 30, 2928; 37, 6451.

294. Bror Holmberg, (a) Arkiv Kemi, Mineral. Geol., 6, No. 1, 1-20 (1915); (b) *ibid.*, 12A, No. 9, 11 p. (1936); (c) *ibid.*, No. 14, 10 p. (1937); (d) *ibid.*, 15A, No. 8, 1-15 (1942); (e) *ibid.*, 17A, No. 23, 10 p. (1944); (f) *ibid.*, B20, No. 2, 8 p. (1945)—C.A. 10, 1187; 30, 3424; 31, 4292; 37, 85; 39, 4065; 41, 2001.
295. Bror Holmberg, (a) J. prakt. Chem., [2] 71, 264-95 (1905); (b) *ibid.*, 75, 169-87 (1907); (c) *ibid.*, 84, 634-86 (1911); (d) *ibid.*, 135, 57-100 (1932); (e) *ibid.*, 141, 93-112 (1934); Ing. Vetenskaps Akad., Handl. No. 131, 85 p. (1934)—C.A. 1, 1845; 6, 985; 27, 704; 29, 783, 1136.
296. Bror Holmberg, (a) Z. anorg. Chem., 56, 385 (1907-8); (b) Ing. Vetensk. Akad., Handl. No. 103, 5-75 (1930); (c) Svensk Pappers-Tid., 34, 835-8 (1931); (d) *ibid.*, 33, 679-86 (1930); *ibid.*, 34, 215-7 (1931); Papier-Fabr., 36, Tech.-Wiss. T1. 218-23 (1938); (e) Oesterr. Chemiker-Ztg. 43, 152-8 (1940)—C.A. 2, 1691; 25, 4393; 26, 2968; 24, 6007; 25, 4121; 32, 6858; 35, 88.
297. Bror Holmberg and Nils Gralén, Ing. Vetenskaps Akad., Handl. No. 162, 29 p. (1942)—C.A. 37, 6451.
298. Bror Holmberg and K. J. Lenander, Arkiv Kemi, Mineral. Geol., 6, No. 17 (1917)—C.A. 12, 807.
299. Bror Holmberg and Karl Mattisson, Ann., 353, 123-30 (1907)—C.A. 1, 2233.
300. Bror Holmberg and A. Ohlsson, Svensk Pappers-Tid., 34, 647-52 (1931)—C.A. 26, 1776.
301. Bror Holmberg and Edmund Schjånberg, Arkiv Kemi, Mineral. Geol., 14A, No. 7, 22 p. (1940)—C.A. 35, 2113.
302. Peter Holtz, Z. physiol. Chem., 250, 87-103 (1937)—C.A. 32, 1263.
303. Peter Holtz and G. Triem, (a) Z. physiol. Chem., 248, 1-4 (1937); (b) *ibid.*, 5-20—C.A. 31, 6617, 6618.
304. H. Hoog and E. Eichwald, Rec. trav. chim., 58, 481-92 (1939)—C.A. 33, 7535.
305. I. V. Hopper, J. H. MacGregor, and F. J. Wilson, J. Soc. Dyers Colourists, 57, 6-9 (1941)—C.A. 35, 2484.
306. E. M. Hoshall, J. Assoc. Official Agr. Chem., 23, 727-34 (1940)—C.A. 35, 279.
307. J. Houben, Ber., 45, 2942-6 (1912)—C.A. 7, 1005.
308. Richard Hueter to Deutsche Hydrierwerke, U.S. pat. 2,113,807 (1938)—C.A. 32, 4251.
309. H. M. Huffman and E. L. Ellis, J. Am. Chem. Soc., 57, 46-8 (1935)—C.A. 29, 2065.

310. R. A. Hummel and E. B. Sandell, *Anal. Chim. Acta*, **7**, 308–12 (1952)—C.A. **47**, 4785.
311. George Hunter, *Biochem. J.*, **22**, 4–10 (1928); *Can. J. Research*, **27E**, 230–9 (1949)—C.A. **22**, 1985; **43**, 9140.
312. George Hunter and B. A. Eagles, (a) *J. Biol. Chem.*, **65**, 623–41 (1925); (b) *ibid.*, **72**, 123–32 (1927)—C.A. **20**, 229; **21**, 1995.
313. George Hunter, S. G. Fushtey, and D. W. Gee, *Can. J. Research*, **27E**, 240–3 (1949)—C.A. **43**, 9379.
314. George Hunter, G. D. Molnar, and N. J. Wight, *Can. J. Research*, **27E**, 226–9 (1949)—C.A. **43**, 9378.
315. J. H. Hunter and B. E. Leach to Upjohn Co., U.S. pat. 2,480,079 (1949)—C. A. **44**, 2569.
316. I. G. Farben., (a) Fr. pat. 766,056 (1934); Ger. pat. 642,378 (1937); (b) Brit. pat. 247,986 (1925); (c) 432,480 (1935); (d) Belg. pat. 448,962 (1943)—C.A. **28**, 6723; **31**, 3496; **21**, 594; **30**, 106; **42**, 209.
317. E. P. Irany and H. D. Noether to Celanese Corp. of America, U.S. pat. 2,481,596 (1949)—C.A. **43**, 9527.
- 317.5. Kanetsugu Ishii, *J. Japan. Biochem. Soc.*, **24**, 118–22 (1952–53)—C.A. **47**, 12125.
318. G. Ivanovics and L. Vargha, *Z. physiol. Chem.*, **281**, 156–62 (1944)—C.A. **42**, 3757.
319. Martin Jacoby, *Biochem. Z.*, **259**, 211–22 (1933)—C.A. **27**, 2701.
320. T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 442–50 (1939)—C.A. **33**, 2498.
321. E. F. Jansen, *J. Biol. Chem.*, **176**, 657–64 (1948)—C.A. **43**, 2580.
322. E. F. Jansen to the U.S.A. as represented by the Sec'y. of Agr., U.S. pat. 2,539,428, 2,559,625 (1951)—C.A. **45**, 7588, 10,258.
323. J. E. Jansen to B. F. Goodrich Co., U.S. pat. 2,468,982 (1949)—C.A. **43**, 5424.
324. Hjalmar Johansson, *Lunds Universitets Arsskift N. F. Avd.* **2**, **12**, No. 8—C.A. **11**, 2576.
325. T. B. Johnson and A. J. Hill, *Am. Chem. J.*, **45**, 356–67 (1911)—C.A. **5**, 2071.
326. F. A. Jones, *Trans. Inst. Rubber Ind.*, **17**, 133–8 (1941)—C.A. **36**, 2441.
327. J. H. Jones, *J. Assoc. Official Agr. Chem.*, **27**, 574–6 (1944)—C.A. **39**, 1509.

- 328. Edward Kaczka and Karl Folkers, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 243–268.
- 329. E. A. Kaczka, J. F. McPherson, Ralph Mazingo, and Karl Folkers to Merck & Co., Inc., U.S. pat. 2,489,894 (1949)—C.A. 44, 1531.
- 330. Kärnbolaget Aktiebolag (B. A. L. Holmberg), Swed. pat. 94,910 (1939)—C.A. 33, 5870.
- 331. Kalle & Co., Ger. pat. 180,875 (1905)—C.A. 1, 1656.
- 331.5. Kalle & Co. (Oskar Süs), (a) Ger. pat. 831,997 (1952); (b) 831,998 (1952)—C.A. 47, 2201, 6978.
- 332. Sten Kallenberg, (a) *Svensk Kem. Tid.*, 29, 53–5 (1917); (b) *Ber.*, 52, 2057–71 (1919)—C.A. 11, 2467; 14, 1994.
- 333. Shu Kambara and Akira Hayashi, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, 54, 68–70 (1951)—C.A. 47, 1419.
- 334. P. Karrer with Rosa Baumgarten, S. Gunther, W. Harder, and Lina Lang, *Helv. chim. acta*, 4, 130–48 (1921)—C.A. 15, 2631.
- 335. Tako Kato, Kijiro Arikawa, and Takezo Sasaki, *Bunseki to Shiyaku*, 3, 159–64 (1950)—C.A. 46, 10,044.
- 336. J. R. Katz, J. Seiberlich, and A. Weidinger, *Biochem. Z.*, 298, 323–5 (1938)—C.A. 33, 23.
- 336.5. Leon Katz, L. S. Karger, William Schroeder, and M. S. Cohen, *J. Org. Chem.*, 18, 1380–1402 (1953)—C.A. 48, 12034.
- 337. S. Keimatsu, K. Yokota, and I. Satoda, *J. Pharm. Soc. Japan*, 52, 531–42 (1932)—C.A. 26, 4800.
- 337.5. W. R. Keithler, *Drug & Cosmetic Ind.*, 73, 180–1 (1953)—C.A. 48, 332.
- 338. E. C. Kendall and F. F. Nord, *J. Biol. Chem.*, 69, 295–337 (1926)—C.A. 20, 3446.
- 339. M. S. Kharasch, (a) U.S. pat. 1,589,599 (1926); (b) 1,672,615 (1928); (c) 1,677,392 (1928)—C.A. 20, 3061; 22, 2639, 3265.
- 340. M. S. Kharasch to Eli Lilly & Co., (a) U.S. pat. 1,684,920 (1928); (b) 2,130,321 (1938)—C.A. 22, 4538; 32, 9098.
- 341. M. S. Kharasch and H. S. Isbell, *J. Am. Chem. Soc.*, 53, 2701–3 (1931)—C.A. 25, 4220.
- 342. M. S. Kharasch, Alice T. Read and F. R. Mayo, *Chemistry & Ind.*, 1938, 752—C.A. 32, 8379.
- 342.5. L. C. King and F. H. Suydam, *J. Am. Chem. Soc.*, 74, 5499–5501 (1952)—C.A. 48, 3255.
- 343. Frank Kipnis, Isidore Levy, and John Ornfelt, *J. Am. Chem. Soc.*, 71, 2270–1 (1949)—C.A. 43, 7014.

344. Peter Klason, (a) *Ann.*, 187, 113–26 (1877); (b) *Ber.*, 14, 409–10 (1881).
345. Peter Klason and Tor Carlson, *Ber.*, 39, 732–8, 738–42 (1906).
346. Robert Klement, *Ber.*, 66, 1312–5 (1933)—*C.A.* 28, 62.
347. Robert Klement and Albert May, *Ber.*, 71, 890–4 (1938)—*C.A.* 32, 6640.
348. H. L. Klug and D. F. Petersen, *Proc. S. Dakota Acad. Sci.*, 28, 87–91 (1949)—*C.A.* 46, 900.
349. G. Kögel, *Phot. Ind.*, 29, 126–8 (1931); *Sci. ind. phot.*, [2] 2, 131–2 (1931)—*C.A.* 26, 5857.
350. C. F. Koelsch, *J. Am. Chem. Soc.*, 52, 1105–8 (1930)—*C.A.* 24, 1843.
351. Otto König and W. R. Crowell, *Mikrochemie ver Mikrochim. Acta*, 33, 300–2 (1948)—*C.A.* 42, 6263.
352. Yasuo Koseki and Mitsunori Ishida, *Bull. Soc. Sci. Phot. Japan*, Aug., 1951, 1723; *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 53, 312–13 (1950)—*C.A.* 46, 6977, 10,983.
353. M. M. Koton, *J. Gen. Chem. (USSR)*, 22, 643–7, 705–8 (Engl. trans.) (1952)—*C.A.* 47, 5376; 48, 2660.
354. Henry Kramer, *J. Assoc. Offic. Agr. Chemists*, 35,* 285–7 (1952)—*C.A.* 46, 11,590.
- 354.5. K. G. Krebs and W. Lang, *Krankenhaus-Apoth. (Suppl. Deut. Apoth. Ztg.)*, 1951, 18—*C.A.* 48, 2323.
355. J. H. Krepelka and Z. Rézö, *Coll. Czech. Chem. Com.*, 10, 559–81 (1938)—*C.A.* 33, 2485.
356. Sri Krishna and Sajjan Singh, *Quart. J. Indian Chem. Soc.*, 4, 291–6 (1927)—*C.A.* 22, 1150.
357. H. H. Kroll, R. A. Arens, S. Mesirov, S. F. Strauss, and H. Necheles, *Surgery*, 11, 810–4 (1942)—*C.A.* 36, 4907.
358. Shoji Kubo, *J. Chem. Soc. Japan*, 72, 535–6 (1951)—*C.A.* 46, 7086.
359. Tozaburo Kurihara and Jiro Kitamura, *J. Pharm. Soc. Japan*, 72, 76–8 (1952)—*C.A.* 46, 11,150.
360. Junzo Kurosawa, *Bull. Research Inst. S. Manchurian Rwy. Co.*, 12, 91–130 (1928)—*C.A.* 23, 2202.
361. Koji Kuroyanagi and Ichiro Sakurada, *Chem. High Polymers (Japan)*, 7, 255–7 (1950)—*C.A.* 46, 10,103.
362. Marcel Labbé and F. Nepveux, *Compt. rend.*, 192, 1061–2 (1931)—*C.A.* 25, 4041.
363. R. Labes, *Arch. Exptl. Path. Pharm.*, 41, 148–60 (1929)—*C.A.* 24, 2180.

364. H. Lagodsky, *Bull. soc. path. exotique*, *31*, 234-44 (1938)—C.A. 32, 8003.
365. M. R. Lalic, *Bull. soc. chim. Belgrade*, *11*, 58-62 (1940-6)—C.A. 42, 2894.
366. U. Lampert and P. Wels, *Arch. exptl. Path. Pharmacol.*, *175*, 554-7 (1934)—C.A. 28, 6733.
367. N. A. Langlet, *Ber.*, *24*, 3848-53 (1891).
368. Erik Larsson, (a) *Z. anorg. allgem. Chem.*, *172*, 375-84 (1928); (b) *Ber.*, *61*, 1439-43 (1928); (c) *Z. anal. Chem.*, *79*, 170-5 (1929); (d) *Trans. Chalmers Univ. Technol.*, Gothenburg, Sweden, No. 35, 3-17 (1944)—C.A. 22, 4318, 4470; 24, 1057; 39, 2488.
369. Erik Larsson, (a) *Svensk Kem. Tid.*, *40*, 149-50 (1928); (b) *ibid.*, *45*, 65-72 (1933); (c) *ibid.*, *52*, 9-15 (1940); (d) *ibid.*, *55*, 168-71 (1943)—C.A. 27, 3384; 34, 4054; 38, 5798, 6275.
370. Leon Launoy, *Compt. rend.*, *199*, 646-8 (1934); *Bull. soc. chim. biol.*, *17*, 1022-30 (1935)—C.A. 29, 222, 6946.
371. W. M. Lauter, A. E. Jurist, and W. G. Christiansen, *J. Am. Pharm. Assoc.*, *22*, 212-4 (1933)—C.A. 27, 4026.
372. Alexander Lawson, H. V. Morley, and L. I. Woolf, (a) *Biochem. J.*, *47*, 513-18 (1950); (b) *Nature*, *167*, 82-3 (1951)—C.A. 45, 3015, 8010.
373. W. A. Lazier, A. A. Pavlic, and W. J. Peppel to Du Pont Co., U.S. pat. 2,422,246 (1947)—C.A. 41, 6277.
374. W. A. Lazier and F. W. Signaigo to Du Pont Co., U.S. pat. 2,402,639 (1946)—C.A. 40, 5764.
375. W. A. Lazier, F. K. Signaigo, and J. H. Werntz, U.S. pat. 2,402,644 (1946)—C.A. 40, 5765.
- 375.5. J. B. Lear and M. G. Mellon, *Anal. Chem.*, *25*, 1411-2 (1953)—C.A. 48, 4.
376. Otto Leberl, *Austrian pat.* 169,458 (1951)—C.A. 46, 11597.
377. R. R. Legault, A. B. Wilder, and R. W. Gerard, *J. Biol. Chem.*, *113*, 537-55, 557-69 (1936)—C.A. 30, 3841.
378. J. U. Lerch, *Ann.*, *124*, 39-40 (1862).
- 378.3. D. L. Leussing, *Univ. Microfilms (Ann Arbor, Mich.)*, Pub. No. 5359, 161 p.; *Dissertation Abstrs.*, *13*, 469-70 (1953)—C.A. 47, 12090.
- 378.5. D. L. Leussing and I. M. Kolthoff, (a) *J. Electrochem. Soc.*, *100*, 334-8 (1953); (b) *J. Am. Chem. Soc.*, *75*, 3904-11 (1953)—C.A. 47, 12041, 12090.

379. P. A. Levene and L. A. Mikeska, (a) *J. Biol. Chem.*, **60**, 1-3 (1924); *ibid.*, **63**, 85-93 (1925); (b) *ibid.*, **60**, 685-92 (1924); (c) *ibid.*, **70**, 365-80 (1926)—C.A. **18**, 2494; **19**, 1245, 1130; **21**, 52.
380. P. A. Levene and T. Mori, *J. Biol. Chem.*, **78**, 1-22 (1928)—C.A. **22**, 2739.
381. P. A. Levene, Alexandre Rothen, and Martin Kuna, *J. Biol. Chem.*, **121**, 747-59 (1937)—C.A. **32**, 917.
382. M. J. Lewenstein, U.S. pat. 2,518,154 (1950)—C.A. **45**, 657.
383. Leon Libenson, *Exptl. Med. Surg.*, **3**, 146-53 (1945)—C.A. **39**, 5334.
384. D. Libermann, J. Himbert, and L. Hengl, *Bull. soc. chim. France*, **1948**, 1120-4—C.A. **43**, 3819.
385. Carl Liebermann and A. Lange, *Ber.*, **14**, 1265-6 (1881); *Ann.*, **207**, 131-37 (1881).
386. Ch'wan-Kwang Lin, *Plant Physiol.*, **21**, 304-18 (1946)—C.A. **40**, 6575.
387. B. H. Lincoln and G. D. Byrkit to Continental Oil Co., U.S. pat. 2,257,752 (1941)—C.A. **36**, 894.
388. E. S. Loeffler and W. M. Hoskins, *J. Econ. Entomol.*, **39**, 589-97 (1946)—C.A. **21**, 2526.
389. J. S. Long and W. S. Egge, *Ind. Eng. Chem.*, **20**, 809-11 (1928)—C.A. **22**, 3540.
390. S. A. Lough and H. B. Lewis, *J. Biol. Chem.*, **104**, 601-10 (1934)—C.A. **28**, 3715.
391. J. M. Loven, (a) *J. prakt. Chem.*, [2] **29**, 366-78 (1884); (b) *ibid.*, **33**, 101-5 (1886); (c) *ibid.*, **47**, 173-82 (1893); (d) *ibid.*, **78**, 63-73 (1908)—C.A. **3**, 73.
392. J. M. Loven and Hjalmar Johansson, *Ber.*, **48**, 1254-62 (1915)—C.A. **9**, 2650.
393. C. C. Lucas and E. J. King, *Biochem. J.*, **27**, 2076-89 (1932)—C.A. **27**, 3164.
394. Edward Lyons, (a) *J. Am. Chem. Soc.*, **49**, 1916-20 (1927); (b) U.S. pat. 1,644,258 (1927)—C.A. **21**, 3581, 3906.
395. C. P. McCord, *Ind. Med.*, **15**, 669-76 (1946)—C.A. **41**, 7514.
396. R. Maly and Rudolph Andreasch, *Ber.*, **13**, 601-7 (1880).
397. R. E. Mark, *Biochem. Z.*, **154**, 43-8 (1924)—C.A. **19**, 1867.
398. H. M. Martin to Martin Labs. Inc., U.S. pat. 2,413,361 (1946)—C.A. **41**, 1698.

- 398.5. V. F. Martynov and N. A. Rozepina, *J. Gen. Chem* (USSR), **22**, 1577-80 (1952)—C.A. **47**, 8016.
399. A. P. Mathews and Sydney Walker, *J. Biol. Chem.*, **6**, 21-8, 29-37 (1909)—C.A. **3**, 2172.
400. May & Baker, Ltd., H. J. Barber, and Ronald Slack, *Brit. pat.* 585,581 (1947)—C.A. **45**, 9077.
401. May & Baker, Ltd., A. J. Ewins, and George Newbery, *Brit. pat.* 475,042 (1937)—C.A. **32**, 3556.
402. May & Baker, Ltd., Glaxo Laboratories, Ltd., H. J. Barber, Ronald Slack, C. E. Stickings, D. E. Elliott, and John Attenburrow, *Brit. pat.* 585,089 (1947)—C.A. **41**, 3822.
403. Fritz Mayer, (a) *Ber.*, **42**, 1132-7 (1909); (b) *ibid.*, **43**, 584-96 (1910)—C.A. **3**, 2129; **4**, 1303.
404. R. L. Mayer, *Bull. acad. med.*, **115**, 670-2 (1936)—C.A. **31**, 3992.
405. C. Mayr and A. Gebauer, *Z. anal. Chem.*, **113**, 189-211 (1938)—C.A. **32**, 7843.
406. Medical Research Committee, Washington, and Medical Research Council, London, *Science*, **102**, 627-9 (1945)—C.A. **40**, 2146.
407. J. P. Mehlig and M. J. Shepherd, Jr., *Chemist Analyst*, **35**, 8-14 (1946)—C.A. **40**, 2410.
408. Merck & Co., (a) *Brit. pat.* 622,298 (1949); (b) 670,495 (1951)—C.A. **43**, 7039; **46**, 7593.
409. F. O. W. Meyer, *Pharm. Zentralhalle*, **89**, 3-8 (1950)—C.A. **44**, 6770.
410. Otto Meyerhof, (a) *Arch. ges. Physiol. (Pfluger's)*, **170**, 428-75 (1918); (b) *ibid.*, **200**, 1-10 (1923)—C.A. **13**, 2056; **18**, 91.
411. Leonor Michaelis and E. S. G. Barron, *J. Biol. Chem.*, **83**, 191-210 (1929)—C.A. **23**, 4954.
412. Leonor Michaelis and M. P. Schubert, *J. Am. Chem. Soc.*, **52**, 4418-26 (1930)—C.A. **25**, 77.
413. Leonor Michaelis and S. Yamaguchi, *J. Biol. Chem.*, **83**, 367-73 (1929)—C.A. **23**, 5207.
414. L. P. Miller, *Contrib. Boyce Thompson Inst.*, **3**, 309-12 (1931)—C.A. **25**, 5445.
415. K. A. H. Mörner, (a) *Z. physiol. Chem.*, **42**, 349-64 (1904); (b) *ibid.*, 365-70.
416. E. E. Moore to Abbott Labs., *U. S. pat.* 2,509,198 (1950)—C.A. **44**, 9478.
417. E. E. Moore and R. T. Rapala, *J. Am. Chem. Soc.*, **69**, 266 (1947)—C.A. **41**, 3758.

418. Jean Morelle, *Soap, Perfumery & Cosmetics*, 25, 828–33 (1952); *Ind. Parfum.*, 7, 201–4 (1952)—C.A. 47, 272, 822.
419. Sergius Morgulis and D. E. Green, *Protoplasma*, 14, 161–9 (1931)—C.A. 26, 1037.
420. C. W. Mortenson to Du Pont Co., U.S. pat. 2,443,923 (1948); 2,476,891 (1949)—C.A. 42, 7108; 43, 9081.
421. Ralph Mozingo and Karl Folkers, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 535–656—C.A. 44, 9419.
422. Ralph Mozingo, Karl Folkers, and N. R. Easton to Merck & Co., Inc., U.S. pat. 2,515,465 (1950)—C.A. 44, 8950.
423. Ralph Mozingo, J. F. McPherson, and Karl Folkers to Merck & Co., Inc., (a) Brit. pat. 638,513 (1950); U.S. pat. 2,516,240 (1950); (b) 2,539,854 (1951)—C.A. 44, 8365; 45, 666, 7602.
- 435.5. Karl Mülhens, *Seifen-Öle-Fette-Wachse*, 78, 417–8 (1952)—C.A. 47, 7165.
424. Eugen Mueller to Winthrop Chem. Co., U.S. pat. 2,111,151 (1933)—C.A. 32, 3557.
425. J. F. Mulvaney, *Proc. Sci. Sect. Toilet Goods Assoc.*, 5, 33 (1946)—C.A. 40, 7162.
426. J. F. Mulvaney and R. L. Evans, *Proc. Sci. Sect. Toilet Goods Assoc.*, 7, 32–4 (1947); *Am. Perfumer*, 50, 33–5—C.A. 41, 5095, 7056.
427. C. N. Myers, *J. Lab. Clin. Med.*, 6, 359–73 (1921)—C.A. 15, 2274.
428. R. Neher, M. Spillmann, L. H. Werner, A. Wettstein, and K. Miescher, *Helv. chim. acta*, 29, 1874–82 (1946)—C.A. 41, 2037.
429. I. R. Neher, A. Wettstein, and K. Miescher, *Helv. chim. acta*, 29, 1815–29 (1946)—C.A. 41, 2036.
430. Carl Neuberg, *Ber.*, 35, 3161–4 (1902).
431. A. Neuberger, *Biochem. J.*, 32, 1452–6 (1938)—C.A. 32, 9040.
432. Eleanor B. Newton, S. R. Benedict, and H. D. Dakin, *Science*, 64, 602 (1926); *J. Biol. Chem.*, 72, 367–73 (1927)—C.A. 21, 590, 1995.
433. B. H. Nicolet, *J. Am. Chem. Soc.*, 53, 3066–72 (1931)—C.A. 25, 4850.
434. B. H. Nicolet and L. F. Bate, *J. Am. Chem. Soc.*, 49, 2064–8 (1927)—C.A. 21, 3045.
435. B. H. Nicolet and L. A. Shinn, *J. Am. Chem. Soc.*, 63, 2284–5 (1941)—C.A. 35, 6461.

- 435.5. L. H. Noda, S. A. Kuby, and H. A. Lardy, *J. Am. Chem. Soc.*, **75**, 913-7 (1953)—C.A. **48**, 1260.
436. Nordmark-Werke G.m.b.H., *Ger. pat.* 804,808 (1951)—C.A. **45**, 8034.
437. W. J. Nungester, Mary N. Hood, and Mary K. Warren, *Proc. Soc. Exptl. Biol. Med.*, **52**, 287-9 (1943)—C.A. **37**, 3880.
438. Tamio Omori, *J. Biochem. (Japan)*, **16**, 483-97 (1932)—C.A. **27**, 1021.
439. Shinsuke Ose, Yoshio Yoshimura, Isaburo Matsumoto, Shoji Moriguchi, and Tsuneo Usui, *J. Pharm. Soc. Japan*, **70**, 701-3, 704-7 (1950)—C.A. **45**, 6628.
440. Wilhelm Ostwald, *Z. physik. Chem.*, **3**, 170-97 (1889).
441. A. Oteiza y Sentien and E. P. Farinas y Guevara, *Vida Nueva, Havana*, 1937, No. 1; *Urol. Cutaneous Rev.*, **41**, 355 (1937)—C.A. **31**, 4723.
442. Emil Ott and E. E. Reid, *Ind. Eng. Chem.*, **22**, 884-6 (1930)—C.A. **24**, 4758.
- 442.5. G. Ottaviano, *Boll. soc. ital. biol. sper.*, **25**, 969-70 (1950)—C.A. **46**, 5124.
443. B. L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 1949, 3109-13—C.A. **44**, 4864.
444. E. P. Painter, *Chem. Rev.*, **28**, 179-213 (1941)—C.A. **35**, 5508.
445. C. Pak and B. E. Read, *Chinese J. Physiol.*, **14**, 375-88 (1939)—C.A. **34**, 4811.
446. Parke, Davis & Co., (a) *Brit. pat.* 331,195 (1928); (b) 444,882 (1936)—C.A. **25**, 173; **30**, 6513.
447. Jacques Parrod, (a) *Compt. rend.*, **215**, 146-8 (1942); *ibid.*, **224**, 839-42 (1947); (b) *ibid.*, **218**, 599-600 (1944)—C.A. **38**, 4906; **42**, 522; **40**, 2436.
448. W. I. Patterson, W. B. Geiger, L. R. Mizell, and Milton Harris, *J. Research Natl. Bur. Standards*, **27**, No. 1, 89-103 (1941) (Research Paper No. 1405); *Textile Research*, **11**, 379-93 (1941)—C.A. **35**, 6800.
449. A. A. Pavlic to Du Pont Co., *U.S. pat.* 2,408,094 (1946)—C.A. **41**, 775.
450. R. L. Peck and Karl Folkers, (a) *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 52-75; (b) *ibid.*, 144-206—C.A. **44**, 9414, 9415.
451. W. J. Peppel to Du Pont Co., *U.S. pat.* 2,408,095 (1946)—C.A. **41**, 776.

452. J. J. Perez and G. Sandor, *Bull. soc. chim. biol.*, **33**, 149–52 (1940)—C.A. **34**, 5826.
453. P. Petrenko-Kritchenko, A. Ravikovich, V. Opotskii, E. Putgatui, and M. Diakovo, *J. Russ. Phys. Chem. Soc.*, **60**, 149–52 (1928)—C.A. **22**, 3575.
454. M. Picon, *J. pharm. chim.*, **21**, 215–25 (1935)—C.A. **29**, 7500.
455. N. W. Pirie, (a) *Biochem. J.*, **25**, 614–28 (1931); (b) *ibid.*, 1565–79; (c) *ibid.*, **27**, 202–5 (1933); (d) *ibid.*, 1181–8—C.A. **25**, 4850; **26**, 1504; **27**, 3962; **28**, 959.
456. N. W. Pirie and T. S. Hele, *Biochem. J.*, **27**, 1716–8 (1933)—C.A. **28**, 2399.
457. H. M. Powell and R. M. Rice, *J. Lab. Clin. Med.*, **29**, 372–4 (1944)—C.A. **38**, 5955.
- 457.5. D. H. Powers and G. Barnett, *J. Soc. Cosmetic Chemists*, **4**, 92–100 (1953)—C.A. **48**, 2329.
458. B. C. Pratt to Du Pont Co., U.S. pat. 2,461,920 (1949)—C.A. **43**, 4290.
459. P. W. Preisler and Doris B. Priesler, *J. Biol. Chem.*, **89**, 631–45 (1930); *ibid.*, **95**, 181–8 (1932)—C.A. **25**, 894; **26**, 2702.
460. W. S. Preston, W. D. Block, and R. H. Freyberg, *Proc. Soc. Exptl. Biol. Med.*, **50**, 253–6 (1942)—C.A. **36**, 5253.
- 460.5. Fosco Provvedi and Silvio Camozzo, *Chimica e industria (Milan)*, **34**, 517–9 (1952)—C.A. **47**, 4046.
461. G. R. Ramage and Imperial Chemical Industries Ltd., *Brit. pat.* 591,381 (1947)—C.A. **42**, 923.
462. Ludwig Ramberg, *Ber.*, **39**, 1356–8 (1906).
463. J. C. Ransmeier and J. A. Stekol, *Proc. Soc. Exptl. Biol. Med.*, **51**, 85–8 (1942)—C.A. **37**, 404.
464. Lorence Rapoport, Allen Smith, and M. S. Newman, *J. Am. Chem. Soc.*, **69**, 693–4 (1947)—C.A. **41**, 4102.
465. Sarah Ratner and H. T. Clarke, *J. Am. Chem. Soc.*, **59**, 200–6 (1937)—C.A. **31**, 1362.
466. G. B. Reed and J. H. Orr, *Proc. Soc. Exptl. Biol. Med.*, **48**, 535–40 (1941)—C.A. **36**, 1057.
- 466.5. L. J. Reed and Ching-I Niu, *J. Am. Chem. Soc.*, **77**, 416–9 (1955)—C.A. **49**, 5288.
467. E. Emmet Reid—Personal observation.
468. R. D. Reid and Gertrude H. Bowditch, *J. Lab. Clin. Med.*, **27**, 671–3 (1942)—C.A. **36**, 2289.
469. L. Reiner and C. S. Leonard, *Arch. intern. pharmacodynamie*, **43**, 49–62 (1932)—C.A. **27**, 3002.

470. J. A. Reuterskiöld, Uppsala (Appelborgs Boktryckeriaktiebolag), 1939, 272 p. (separate)—C.A. 34, 2791.
471. Heinrich Rheinboldt, Franz Tappermann, and Hans Kleu, *J. prakt. Chem.*, [2] 153, 65–76 (1939)—C.A. 33, 6279.
472. G. M. Richardson, *Biochem. J.*, 27, 1036–9 (1933)—C.A. 28, 397.
473. Fritz Richter, *Chem. Tech.*, 1, 31–4 (1949)—C.A. 44, 973.
474. Hermann Richtzenhain, *Ber.*, 72, 2152–60 (1939)—C.A. 34, 3270.
475. Byron Riegel and Vincent du Vigneaud, *J. Biol. Chem.*, 112, 149–54 (1935)—C.A. 30, 2175.
- 475.5. J. J. Ritter and M. J. Lover, *J. Am. Chem. Soc.*, 74, 5576–7 (1952)—C.A. 48, 568.
476. W. C. Rose and E. E. Rice, *J. Biol. Chem.*, 130, 305–23 (1939)—C.A. 33, 8718.
477. Arthur Rosenheim, *Z. anorg. Chem.*, 57, 359–60 (1908)—C.A. 2, 1692.
478. Arthur Rosenheim and Isser Davidsohn, *Z. anorg. Chem.*, 41, 231–48 (1904).
479. Arthur Rosenheim and Wilhelm Stadler, *Ber.*, 38, 2687–90 (1905).
480. Sidney Rothbard, D. M. Angevine, and R. L. Cecil, *J. Pharmacol.*, 72, 164–75 (1941)—C.A. 35, 5988.
481. K. Rothstein, *Ber.*, 58, 53–6 (1925)—C.A. 19, 1407.
482. C. A. Rouiller, *J. Am. Chem. Soc.*, 41, 777–81 (1919); *Proc. Nat. Acad. Sci.*, 5, 145—C.A. 13, 2031.
483. J. I. Routh, *J. Biol. Chem.*, 130, 297–304 (1939)—C.A. 33, 9285.
484. L. G. Rowntree and J. J. Abel, *J. Pharmacol.*, 2, 101–43—C.A. 5, 1618.
- 484.5. T. Rumele and G. T. Walker, *Soap, Perfumery & Cosmetics*, 26, 461–2 (1953)—C.A. 47, 10178.
485. P. Rumpf, *Bull. soc. chim.*, [5] 9, 661–7 (1942)—C.A. 38, 2951.
486. John Runnström, Astri Runnström, and Erik Sperber, *Naturwissenschaften*, 25, 540 (1937)—C.A. 31, 8590.
487. L. R. Rykkan and C. L. A. Schmidt, (a) *Univ. Calif. Pub. Physiol.*, 8, 257–76 (1944); (b) *Arch. Biochem.*, 5, 89–98 (1944)—C.A. 38, 2974; 39, 2769.
488. A. B. Sabin, *Proc. Staff Meetings Mayo Clinic*, 17, 542–4 (1942)—C.A. 37, 683.
489. A. B. Sabin and Joel Warren, (a) *J. Bact.*, 40, 823–56 (1940); (b) *Science*, 92, 535–6 (1940)—C.A. 35, 1126, 1520.

490. A. B. Sabin and Joel Warren to The Childrens Hospital, U.S. pat. 2,352,124 (1944)—C.A. 38, 5646.
491. Georg Sachs and Heinrich Blessl, Ber., 58, 1493-9 (1925)—C.A. 20, 183.
492. Georg Sachs and Minna Ott, Monatsh., 47, 415-8 (1926)—C.A. 21, 1257.
493. Seishi Sakuma, Biochem. Z., 142, 68-78 (1923)—C.A. 18, 1838.
494. R. Salechow, Kautschuk, 13, 119-22 (1937)—C.A. 31, 8991.
495. G. Salomone, Bol. Laniera, 43, 992-5 (1929)—C.A. 25, 598.
496. H. B. Salt, Biochem. J., 25, 1712-9 (1931)—C.A. 26, 1655.
497. G. Sartori and A. Liberti, Sbornik Mezinarod. polarog. sjezdu v Praze, 1st Congr., 1951, Pt. I, 250-4 (in Italian)—C.A. 46, 9450.
498. G. Sartori, A. Liberti, and C. Calzolari, Comite intern. thermodynam. et cinet, electrochim., Compt. rend. reunion, 1950, 301-4 (Pub. 1951)—C.A. 46, 10011.
499. B. C. Saunders, Biochem. J., 28, 580-6 (1934)—C.A. 28, 6086.
500. Kenneth Savard, E. M. Richardson, and G. A. Grant, Can. J. Research, 24B, 28-36 (1946)—C.A. 40, 6054.
501. Gino Scagliarini, Atti V. Congr. nazl. chim. pura applicata Rome, 1935, Pt. I, 546-7 (1936)—C.A. 31, 3407.
502. Carl Schacht, Ann., 129, 3-6 (1864).
503. Otto Schales, Ber., 71, 447-60 (1938)—C.A. 32, 3294.
504. Helmuth Scheibler, Ber., 48, 1443-5 (1915)—C.A. 9, 3245.
505. Helmuth Scheibler and Walther Bube, Ber., 48, 1445-61 (1915)—C.A. 9, 3245.
506. Helmuth Scheibler, H. T. Topouzàda, and H. A. Schulze, J. prakt. Chem., [2] 124, 1-28 (1929)—C.A. 24, 1620.
507. Schering-Kahlbaum, (a) Brit. pat. 282,427 (1926); (b) Ger. pat. 472,822 (1927)—C.A. 22, 3736; 23, 2990.
508. Schering-Kahlbaum (Walter Schoeller and H. G. Allardt), Ger. pat. 544,500 (1926)—C.A. 26, 2471.
509. Schering-Kahlbaum (Walter Schoeller and Erich Borgwardt), Ger. pat. 514,506 (1926)—C.A. 25, 1640.
510. Schering-Kahlbaum (Walter Schoeller, Erich Borgwardt, and H. G. Allardt), Ger. pat. 506,443 (1925)—C.A. 25, 381.
511. T. Schinzel and G. Benoit, Bull. soc. chim., [5] 6, 501-9 (1939)—C.A. 33, 5807.

512. Edmund Schjanberg, (a) Svensk Kem. Tid., 53, 282-7 (1941); (b) Ber., 74, 1751-9 (1941); (c) *ibid.*, 75, 468-82 (1942)—C.A. 36, 1902; 37, 2347, 3403.
513. Wilhelm Schmidt-Nickels to Gen. Aniline and Film Corp., U.S. pat. 2,521,676 (1950)—C.A. 45, 8048.
514. S. Schmidt-Nielsen and J. Höye, Kgl. Norske Videnskab. Selskabs, Forh., 15, 99-102 (1942)—C.A. 38, 6553.
515. S. Schmidt-Nielsen and E. Refsnes, Kgl. Norske Videnskab. Selskabs, Forh., 15, 79-82 (1942)—C.A. 38, 6553.
516. Ferdinand Schneider, Biochem. Z., 318, 329-30 (1947)—C.A. 42, 3725.
517. Ferdinand Schneider and Erich Reinefeld, Biochem. Z., 318, 507-14 (1948)—C.A. 43, 137.
- 517.5. E. O. Schnell, U.S. pat. 2,631,965, 2,653,121 (1953)—C.A. 47, 6096, 958.
518. Ellen D. Schock, H. Jensen, and Leslie Hellermann, J. Biol. Chem., 111, 553-9 (1935)—C.A. 29, 8017.
519. Alfons Schöberl, (a) Z. physiol. Chem., 201, 167-90 (1931); (b) *ibid.*, 209, 231-8 (1932); (c) Ann., 507, 111-27 (1933); (d) Ber., 65, 1224-6 (1932); (e) *ibid.*, 70, 1186-93 (1937); (f) Collegium, 1936, 412-21—C.A. 26, 364, 5547; 28, 105; 26, 5069; 31, 5762; 30, 7349.
520. Alfons Schöberl and Friedrich Krumei, (a) Ber., 71, 2361-71 (1938); (b) *ibid.*, 77, 371-7 (1944)—C.A. 33, 964; 40, 4349.
521. Alfons Schöberl and Ernst Ludwig, Ber., 70, 1422-32 (1937)—C.A. 31, 6199.
522. Alfons Schöberl and Annemarie Wagner, Naturwissenschaften, 34, 189 (1947)—C.A. 43, 5742.
523. Walter Schoeller and H. G. Allardt, U.S. pat. 1,683,104 (1928)—C.A. 22, 3959.
524. Walter Schoeller and H. G. Allardt to Schering-Kahlbaum, U.S. pat. 1,689,366 (1928)—C.A. 23, 242.
525. M. P. Schubert, (a) J. Am. Chem. Soc., 53, 3851-6 (1931); (b) *ibid.*, 54, 4077-85 (1932); (c) *ibid.*, 55, 3336-42, 4563-70 (1933); (d) J. Biol. Chem., 111, 671-8 (1935); (e) *ibid.*, 114, 341-50 (1936)—C.A. 26, 92, 5910; 27, 4776; 28, 106; 30, 433, 5940.
526. Franz Schütz, Z. angew. Chem., 46, 780-1 (1933)—C.A. 28, 1021.
527. Werner Schulemann and Fritz Schönhöfer to Winthrop Chem. Co., U.S. pat. 2,041,436 (1936)—C.A. 30, 4512.

528. Ernst Schulze, *Jena Z.*, *I*, 2, 1; 4, 470 (1864)—*Zeit. f. Chemie*, 1865, 73–9.
529. W. F. Schwartz, *J. Pharmacol.*, *65*, 175–84 (1939)—*C.A.* *33*, 2986.
530. G. Schwarzenbach and E. Rudin, *Helv. chim. acta*, *22*, 360–76 (1939)—*C.A.* *33*, 6266.
531. G. E. Serniuk to Standard Oil Dev. Co., U.S. pat. 2,589,151 (1952)—*C.A.* *46*, 5355.
532. G. C. Shattuck, *J. Trop. Med.*, *33*, 33–4 (1930)—*C.A.* *24*, 3272.
- 532.5. M. N. Shchukina and T. V. Gortinskaya, *J. Gen. Chem. (USSR)*, *22*, 1855–61, 1895–1900 (Engl. trans.) (1952)—*C.A.* *47*, 6366; *48*, 4478.
533. J. C. Sheehan, Ralph Mazingo, Karl Folkers, and Max Tishler to Merck & Co., Brit. pat. 627,768 (1949); U.S. pat. 2,477,148 (1949); 2,496,416 (1950)—*C.A.* *44*, 2568, 171, 4510.
534. J. C. Sheehan and Max Tishler to Merck & Co., (a) U.S. pat. 2,477,149 (1949); (b) 2,491,523 (1949)—*C.A.* *44*, 171, 3034.
535. Keita Shibata and Atsushi Watanabe, *Iwata Inst. Plant Biochem. Pub.*, *2*, 97–128 (1936)—*C.A.* *30*, 6277.
536. Kamenosuke Shinohara, (a) *J. Biol. Chem.*, *96*, 285–97 (1932); (b) *ibid.* *109*, 665–79 (1935); *ibid.*, *110*, 263–77 (1935); (c) *ibid.*, *111*, 435–42 (1935); (d) *ibid.*, *112*, 671–82 (1936)—*C.A.* *26*, 4305; *29*, 5141, 5775, 8017; *30*, 2215.
537. R. L. Shriner, J. M. Cross, and E. H. Dobratz, *J. Am. Chem. Soc.*, *61*, 2001–3 (1939)—*C.A.* *33*, 7732.
538. L. E. Shvartsburd and I. A. Soiferman, *Zavodskaya Lab.*, *15*, 387–94 (1949)—*C.A.* *43*, 6940.
539. R. Siemens, *Ber.*, *6*, 659–63 (1873).
540. B. Sjollem and A. Emmerie, *Biochem. Z.*, *204*, 354–60 (1929)—*C.A.* *23*, 1922.
541. G. S. Skinner and J. B. Bicking, *J. Am. Chem. Soc.*, *72*, 1140–1 (1950)—*C.A.* *44*, 6392.
542. Samuel Smiles and D. C. Harrison, *J. Chem. Soc.*, *121*, 2022–6 (1922)—*C.A.* *17*, 85.
543. Samuel Smiles and E. W. McClelland, *J. Chem. Soc.*, *121*, 86–90 (1922)—*C.A.* *16*, 1226.
544. Samuel Smiles and Jessie Stewart, *J. Chem. Soc.*, *119*, 1792–8 (1921)—*C.A.* *16*, 414.

545. P. I. Smith, *Chem. & Met. Eng.*, **53**, No. 9, 98-9 (1946); *Hide and Leather and Shoes*, **112**, No. 8, 14, 20—C.A. **40**, 7678.
546. C. V. Smythe, *J. Biol. Chem.*, **114**, 601-12 (1936)—C.A. **30**, 6399.
547. H. R. Snyder and Wynona Alexander, *J. Am. Chem. Soc.*, **70**, 217-8 (1948)—C.A. **42**, 2252.
548. H. R. Snyder, J. M. Stewart, R. E. Allen, and R. J. Dearborn, *J. Am. Chem. Soc.*, **68**, 1422-8 (1946)—C.A. **40**, 6871.
549. Manoel Soares, *Rev. quim. pura e apl.*, **12**, 1-11 (1937)—C.A. **32**, 3722.
550. Soc. chim. à. Bâle, *Brit. pat.* 533,219 (1941); *Swiss pat.* 210,961 (1940)—C.A. **36**, 495, 3591.
551. Soc. des usines chim. Rhône-Poulenc, *Brit. pat.* 421,989 (1935); *Fr. pat.* 829,219 (1938)—C.A. **29**, 3790; **33**, 1105.
552. H. Sokol and J. J. Ritter, *J. Am. Chem. Soc.*, **70**, 3517-8 (1948)—C.A. **43**, 607.
553. R. C. Sproull and R. A. Lehman, *Am. J. Syphilis, Gonorrhea, Venereal Diseases*, **26**, 166-80 (1942)—C.A. **36**, 3535.
- 553.5. K. H. Sroka, *Seifen-Öle-Fette-Wachse*, **78**, 373-5, 395-6 (1952)—C.A. **47**, 7166.
554. A. Steigmann, *J. Soc. Chem. Ind.*, **61**, 18-9 (1942)—C.A. **36**, 3454.
555. J. A. Stekol, *J. Am. Chem. Soc.*, **64**, 1742 (1942)—C.A. **36**, 5775.
556. C. van der Stelt, W. van der Lugt, and W. T. Nauta, *Rec. trav. chim.*, **70**, 285-8 (1951)—C.A. **45**, 7983.
557. C. van der Stelt, R. F. Rekker, and W. Th. Nauta, *Rec. trav. chim.*, **70**, 675-80 (1951)—C.A. **46**, 3402.
558. Adolph Stern and E. F. Beach, *Proc. Soc. Exptl. Biol. Med.*, **43**, 104-8 (1940)—C.A. **34**, 1938.
559. Jessie Stewart, *J. Chem. Soc.*, **121**, 2555-61 (1922)—C.A. **17**, 545.
560. A. Stoll and E. Seebeck, *Helv. chim. acta*, **32**, 866-76 (1949)—C.A. **43**, 6576.
561. G. G. Stoner and Gregg Dougherty, *J. Am. Chem. Soc.*, **63**, 987-8 (1941)—C.A. **35**, 3604.
- 561.5. J. L. Stoves, *Perfumery Essent. Oil Record*, **43**, 427, 429 (1952)—C.A. **47**, 4038.
562. Walter Strassner, *Biochem. Z.*, **29**, 295-310 (1910)—C.A. **5**, 900.

- 562.5. W. Stricks, I. M. Kolthoff, and A. Heyndrickx, *J. Am. Chem. Soc.*, **76**, 1515-9 (1954)—C.A. **48**, 6898.
563. Oskar Süss, (a) *Ann.*, **559**, 92-101 (1948); (b) *ibid.*, **561**, 31-46 (1948); (c) *ibid.*, **569**, 153-60 (1950)—C.A. **42**, 6320; **43**, 4667; **45**, 1582.
564. Oskar Süss, W. Schafer, and M. Grundkötter, *Ann.*, **571**, 201-25 (1951)—C.A. **45**, 8007.
565. M. X. Sullivan, *Proc. Am. Soc. Biol. Chem.*, *J. Biol. Chem.*, **59**, 1 (1924); *Abstracts Bact.*, **9**, 37 (1925); *U. S. Pub. Health Repts.*, **41**, 1030-56 (1926); *ibid.*, *Suppl.*, No. 78, 13 p. (1929)—C.A. **18**, 3614; **19**, 2834; **20**, 2686; **25**, 2748.
566. M. X. Sullivan and W. C. Hess, *J. Biol. Chem.*, **102**, 67-72 (1933)—C.A. **27**, 5799.
567. F. Suter, *Z. physiol. Chem.*, **20**, 564-82 (1895).
568. A. V. Szent-Györgyi, *Biochem. Z.*, **146**, 245-53, 254-8 (1924)—C.A. **19**, 307.
569. M. L. Tainter, *Proc. Soc. Exptl. Biol. Med.*, **24**, 621 (1927)—C.A. **22**, 2616.
570. Kiyoshi Takahashi, *J. Pharm. Soc. Japan*, **72**, 1148-52 (1952)—C.A. **47**, 6887.
571. R. Tambach, *Ann.*, **280**, 244-5 (1894).
572. Fukuju Tanaka and Masaki Mitsuno, *Ann. Rept. Takeda Research Lab.*, **10**, 65-9 (1951)—C.A. **47**, 4860.
573. S. Tanatar, *J. Russ. Phys. Chem. Soc.*, **43**, 1742-6 (1911)—C.A. **6**, 1279.
574. S. Tanatar and I. Volyanskii, *J. Russ. Phys. Chem. Soc.*, **44**, 1320-4 (1912)—C.A. **7**, 984.
575. C. H. Tanret, *J. pharm. chim.*, [VI] **30**, 145 (1909); *Compt. rend.*, **149**, 222-4 (1909); *Ann. chim. phys.*, [8] **18**, 114-24 (1909)—C.A. **3**, 2679; **4**, 763.
576. Georges Tanret, *Compt. rend.*, **174**, 827-30 (1922); *Bull. soc. chim.*, [4] **31**, 441-8 (1922)—C.A. **16**, 2197.
577. D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1-90 (1951).
- 577.5. D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48-56 (1952)—C.A. **47**, 6338.
578. Sueo Tatsuoka and Masuo Miyamoto, *J. Pharm. Soc. Japan*, **69**, 294-7 (1949)—C.A. **44**, 2513.
579. Sueo Tatsuoka and Masuo Miyamoto to Takeda Drug Mfg. Co., Japan pat. 180,900 (1949)—C.A. **46**, 7585.
580. Sueo Tatsuoka, Masuo Miyamoto, Ujihei Hayashi, and Takashi Tamura to Takeda Drug Mfg. Co., Japan pat. 181,021 (1949)—C.A. **46**, 7585.

581. Sueo Tatsuoka, Masuo Miyamoto, Rin Shiu, and Takashi Tamura, *J. Penicillin (Japan)*, **1**, 382-3 (1947)—C.A. **43**, 2618.
582. Sueo Tatsuoka and Akira Morimoto to Takeda Drug Mfg. Co., Japan pat. 180,987 (1949)—C.A. **46**, 7585.
583. Sueo Tatsuoka, Akira Morimoto, Takashi Tamura, and Tomoji Kinoshita to Takeda Drug Mfg. Co., Japan pat. 3615 (1950)—C.A. **47**, 3338.
584. Sueo Tatsuoka, Takenobu Ueno, and Tomoji Kinoshita, *J. Pharm. Soc. Japan*, **69**, 291-4 (1949)—C.A. **44**, 2512.
- 584.5. Sueo Tatsuoka et al. to Takeda Pharmaceuticals Industries Co., Japan. pat. 5929 (1951)—C.A. **47**, 9999.
585. Sylvia Teich and D. Y. Curtin, *J. Am. Chem. Soc.*, **72**, 2796-8 (1950)—C.A. **45**, 1559.
586. V. N. Thatte and A. S. Ganesan, *Phil. Mag.*, **15**, 51-64 (1933)—C.A. **27**, 3668.
587. Therapeutic Research Corp. of Great Britain Ltd., I. M. Heilbron, and A. H. Cook, (a) *Brit. pat.* 584,813 (1947); (b) 584,918 (1947)—C.A. **41**, 4173, 4175.
588. Therapeutic Research Corp. of Great Britain, Ltd., I. M. Heilbron, A. H. Cook, and J. R. Catch, *Brit. pat.* 607,539 (1948)—C.A. **43**, 4699.
589. K. V. Thimann and W. D. Bonner, Jr., *Am. J. Botany*, **36**, 214-21 (1949)—C.A. **43**, 5094.
590. George Thompson, *J. Soc. Chem. Ind.*, **44**, 196T (1925)—C.A. **19**, 2195.
591. H. W. Thompson, R. R. Brattain, H. M. Randall, and R. S. Rasmussen, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 382-414—C.A. **43**, 8891.
592. Torsten Thunberg, (a) *Skand. Arch. Physiol.*, **25**, 343-5 (1911); (b) *ibid.*, 345-6; (c) *ibid.*, **30**, 385-98 (1913); *Kgl. Fysiograf. S. Lund Handl. (Odenius Festschr.)*, **24**, 1-14—C.A. **6**, 1469, 1447; **8**, 511.
593. Shigeru Toda, *Biochem. Z.*, **172**, 17-30 (1926)—C.A. **20**, 3705.
594. Gerrit Toennies and Mary A. Bennett, *J. Biol. Chem.*, **112**, 497-502 (1936)—C.A. **30**, 2175.
595. S. L. Tompsett, *Biochem. J.*, **28**, 1536-43, 1802-6 (1934)—C.A. **29**, 1447, 1841.
596. Oscar Touster, *J. Biol. Chem.*, **188**, 371-7 (1951)—C.A. **45**, 4296.
597. Roberto Trave and Pietro Colombo, *Gaz. chim. ital.*, **79**, 233-9 (1949)—C.A. **44**, 2919.

598. N. R. Trenner and F. A. Bacher to Merck & Co., (a) U.S. pat, 2,370,592 (1945); (b) 2,370,593 (1945)—C.A. 39, 4730, 3550.
599. H. G. Turley and Wallace Windus to Röhm & Haas Co., U.S. pat. 1,973,130 (1934)—C.A. 28, 7068.
- 599.5. R. B. Turner and Dorothy M. Voitle, J. Am. Chem. Soc., 72, 628-9 (1950)—C.A. 45, 2408.
600. Suzanne Valladas-Dubois, Compt. rend., 231, 53-5 (1950)—C.A. 44, 9853.
601. J. A. Van Allan, J. Am. Chem. Soc., 69, 2914 (1947)—C.A. 42, 1198.
602. W. E. Vaughan and F. F. Rust to Shell Dev. Co., U.S. pat. 2,398,479 (1946)—C.A. 40, 3765.
603. A. G. van Veen and A. J. Hyman, Geneeskund Tijdschr. Nederland. Indie, 73, 991 (1933); Rec. trav. chim., 54, 493-501 (1935)—C.A. 29, 5816.
604. Anatole Vesterman, Proc. XIth Intern. Congr. Pure and Applied Chem., London, 1947, 2, 339-42 (1950)—C.A. 45, 8451.
605. Vincent du Vigneaud, L. F. Audrieth, and H. S. Loring, J. Am. Chem. Soc., 52, 4500-4 (1930)—C.A. 25, 79.
606. Vincent du Vigneaud and F. H. Carpenter, Chemistry of Penicillin (H. T. Clarke et al.), 1949, 1004-1017.
607. Vincent du Vigneaud, F. H. Carpenter, R. W. Holley, A. H. Livermore, and J. R. Rachele, (a) Science, 104, 431-3, 450 (1946); (b) Chemistry of Penicillin (H. T. Clarke et al.), 1949, 1018-24—C.A. 41, 972.
608. Vincent du Vigneaud and R. W. Holley, U.S. pat. 2,543,358 (1951)—C.A. 45, 7601.
609. Vincent du Vigneaud and W. I. Patterson, J. Biol. Chem., 114, 533-8 (1936)—C.A. 30, 5560.
610. Vincent du Vigneaud, W. I. Patterson, and Madison Hunt, J. Biol. Chem., 126, 217-31 (1938)—C.A. 33, 1271.
611. Vincent du Vigneaud, G. W. Stacy, and David Todd, J. Biol. Chem., 176, 907-14 (1948)—C.A. 43, 2581.
612. Vincent du Vigneaud, J. L. Wood, and M. E. Wright, Chemistry of Penicillin (H. T. Clarke et al.), 1949, 892-908.
613. Carl Voegtlin, J. M. Johnson, and H. A. Dyer, J. Pharmacol., 27, 467-83 (1926)—C.A. 20, 2708.
614. Yves Volmar and Ernest Weil, Compt. rend., 207, 534-6 (1938)—C.A. 33, 136.

615. J. H. Waldo, *J. Am. Chem. Soc.*, **53**, 992-6 (1931)—C.A. **25**, 1821.
616. Otto Warburg and Seishi Sakuma, *Arch. ges. Physiol.*, **200**, 203-6 (1923)—C.A. **18**, 815.
617. R. Wegscheider, *Z. physik. Chem.*, **69**, 603-29 (1909)—C.A. **4**, 533.
- 617.5. Bengt Weibull, *Arkiv Kemi, Mineral. Geol.*, **23A**, No. 18, 25 p. (1946)—C.A. **44**, 1427.
618. Rudolf Weidenhagen and Pao-chung Lu, *Z. Wirtschaftsgruppe Zuckerind.*, **86**, Tech. Tl., 240-53 (1936)—C.A. **30**, 6013.
619. Fritz Weigert, *Ber.*, **34**, 3386-3405 (1901).
620. Ulrich Weiss, (a) *J. Am. Chem. Soc.*, **67**, 1424 (1945); (b) *ibid.*, **69**, 2682-4, 2684-7 (1947)—C.A. **39**, 4852; **42**, 1220-1, 3746.
- 620.5. Ulrich Weiss to Endo Prods. Inc., U.S. pat. 2,520,293 (1950); 2,607,789 (1952)—C.A. **46**, 134; **48**, 10552.
621. Arnold Weissberger, C. J. Kibler, and R. V. Young to Eastman Kodak Co., U.S. pat. 2,412,700 (1946)—C.A. **41**, 1701.
622. The Wellcome Foundation Ltd., F. C. Copp, and Samuel Wilkinson, *Brit. pat.* 585,250 (1947)—C.A. **41**, 4175.
623. The Wellcome Foundation Ltd., W. M. Duffin, and Samuel Wilkinson, *Brit. pat.* 585,413 (1947)—C.A. **41**, 4175.
624. L. H. Werner, A. Wettstein, and K. Miescher, *Helv. chim. acta*, **30**, 432-40 (1947)—C.A. **41**, 3056.
625. Abraham White and E. F. Beach, *J. Biol. Chem.*, **122**, 219-26 (1937)—C.A. **32**, 1305.
626. Heinrich Wieland and Wilhelm Franke, (a) *Ann.*, **464**, 101-226 (1928); (b) *ibid.*, **475**, 1-19 (1929)—C.A. **22**, 4320; **24**, 1271.
627. Nils Wigren, *J. prakt. Chem.*, [2] **126**, 246-9 (1930)—C.A. **24**, 4259.
628. D. F. Wilcock and M. M. Sprung to General Electric Co., U.S. pat. 2,597,045 (1952)—C.A. **46**, 9296.
629. P. F. Wiley, *J. Org. Chem.*, **16**, 810-4 (1951)—C.A. **46**, 1481.
- 629.5. P. F. Wiley to Eli Lilly & Co., U.S. pat. 2,606,201 (1952); *Brit. pat.* 694,276 (1953)—C.A. **47**, 6982, 10551.
630. Samuel Wilkinson to Wellcome Foundation Ltd., *Brit. pat.* 585,439 (1947)—C.A. **41**, 3814.
- 630.5. Fritz Will, III, and J. H. Yoe, *Anal. Chem.*, **25**, 1568-71 (1953)—C.A. **48**, 1197.

631. J. W. Williams and E. M. Drissen, *J. Biol. Chem.*, **87**, 441 (1930)—C.A. **24**, 3944.
632. S. W. Williamson and N. U. Meldrum, *Biochem. J.*, **26**, 815-16 (1932)—C.A. **26**, 5593.
633. Oskar Wintersteiner, *J. Biol. Chem.*, **102**, 473-88 (1933)—C.A. **28**, 1066.
634. Oskar Wintersteiner, W. R. Boon, H. C. Carrington, D. W. MacCorquodale, F. H. Stodola, J. L. Wachtel, R. D. Coghill, W. C. Risser, J. E. Philip, and O. Touster, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 76-105.
635. Oskar Wintersteiner, H. E. Stavely, J. D. Dutcher, and M. A. Spielman, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 207-42—C.A. **44**, 9418.
636. Johannes Wislicenius, *Z. f. Chemie*, **1865**, 621-5; *Ann.*, **146**, 145-61 (1868).
637. G. E. Woodward and E. F. Schroeder, *J. Am. Chem. Soc.*, **59**, 1690-4 (1937)—C.A. **31**, 7923.
638. R. B. Woodward, A. Neuberger, and R. N. Trenner, *Chemistry of Penicillin* (H. T. Clarke et al.), 1949, 415-39.
639. L. I. Woolf, *Lancet*, **256**, 757 (1949)—C.A. **43**, 5441.
640. Elizabeth Work, *Lancet*, **256**, 652-4 (1949)—C.A. **43**, 5441.
641. T. Zincke and S. Lenhardt, *Ann.*, **400**, 8 (1913)—C.A. **7**, 3746.

Index

In order to avoid scattering and to bring closely related compounds under one heading, inverted organic names have been used.

For the same reason, it has frequently been necessary to change the name used in the text to a more systematic name.

A

- | | |
|--|--|
| Acetaldehyde, mercapto-, and dimer, 389 | <i>Acetic acid</i> , (antimonydithio)di-, salts, 438, 439 |
| —, thio-, 21 | —, (antimonypentathio)-penta-, 440 |
| Acetamide, 2,2',2''-(antimonytrithio)tri-, 440 | —, (antimonytrithio)tri-, calcium salt, as spirillocide, 439 |
| —, 2,2',2''-(bismuthtrithio)tri-, 440 | —, (arsenictrithio)tri-, 438 |
| —, <i>N</i> -2-mercaptoethyl-2-phenyl-, thiobenzoate, 400 | —, (α -benzoylbenzylthio)-, 446 |
| —, 2-phenyl- <i>N</i> -[2-(phenylacetylthio)ethyl]-, 400 | —, (benzylthio)-, 446 |
| —, mercapto- <i>N</i> -sulfanilyl-, 446 | —, (bismuthdithio)di-, sodium salt, 439 |
| —, <i>N,N'</i> -(thiodiethylene)bis-[2-phenyl-, 400 | —, (<i>tert</i> -butylthio)-, 446 |
| Acetanilide, 2-mercapto-, 294 | —, (cadmiumdithio)di-, cadmium salt, 438 |
| —, 4'-mercapto-, 269 | —, chloro-, thioglycolic acid from, 437 |
| Acetic acid, [<i>p</i> -acetamidophenyl]arsinodithio]di-, 441 | —, (chlorosulphenyl)-, ethyl ester, 269 |
| —, (acetonylthio)-, 390 | —, copperthio-, cupric salt, 440 |
| —, (alkylmercurithio)-, 439 | —, (cyclo-2,5-dithia-3,4-dimethylenestibenylthio)-, 440 |
| —, —, effect on tubercle bacillus, 447 | |
| —, (amidinothio)-, 445 | |

- Acetic acid*, [(dihydroxytin)-dithio]di-, 439
 —, (diphenylarsinothio)-, 441
 —, (1,2-diphenylvinylenedithio)di-, 446
 —, dithiodi-, 447
 —, (ethylenedithio)di-, 441
 —, [(ethylmethylarsino)thio]-, 441
 —, (*p*-hydroxyphenylstibinodithio)di-, 441
 —, (leaddithio)di-, lead salt, 438
 —, mercapto-, 31
 —, (mercuridithio)di-, 438
 —, (α -methylbenzylthio)-, 446
 —, (methylidynetritio)tri-, 445
 —, phenethylthio-, 444
 —, (phenylarsinodithio)di-, 441
 —, (2-phenylphenacylthio)-, 446
 —, [2-(phenylsulfonyl)ethylthio]-, 444
 —, (platinumdithio)di-, 438
 —, (silverthio)-, silver salt, 438
 —, —, sodium salt, 439
 —, sulfo-, thioglycolic acid from, 437
 —, thio-. See *Thioacetic acid*.
 —, thiocyanato-, thioglycolic acid from, 437
 —, thiodi-, thioglycolic acid from, 437
 —, (trichloromethylthio)-, as pressure lubricant, 445
 —, (trimethylenedithio)di-, 441
Acetoacetic acid, esters, reaction with ArSCl , 276
 —, 2,2-bis(ethylthio)-, ethyl ester, 276
Acetoacetic acid, 2-cyano-4-mercapto-, thioacetate and ethyl ester, 445
Acetobromoglucose, reaction with Na thioglycolate, 441
Acetone, reaction with ArSCl , 276
 —, 1,3-dimercapto-, 390
 —, mercapto-, 390, 407
Acetophenone, reaction with ArSCl , 276
 —, *ar*-mercapto-, 391
 —, α -mercapto- α,α -diphenyl-, 390
Acetyl chloride, (4-chloro-2-nitrophenylthio)-, 276
Acetylene, H_2S addition to, 21
Acids, carboxylic, mercaptans from, 38
Acrylonitrile, reaction with H_2S , 21
Adipic acid, 2,4-dimercapto-, 457
 —, 2-mercapto-, 457
Alanine, 3-(*p*-mercapto-phenyl)-, 459
 —, 3,3'-(selenodithio)bis-, 462
 —, 3-sulphenyl-, 265
Albumin, 144
Alcohols, comparison with mercaptans, 15, 16, 111
 —, phys. props. of, 45–48, 50, 52
 —, mercapto-. See *Mercaptans, hydroxy*.
 —, thio-. See *Mercaptans*.
Aldehydes, reactions of, 41, 283, 444
 —, mercapto-, 407
Alkanesulfenic acids, anhydrosulfides with dialkyldithiocarbamic acids, 272
 —, esters, 285

- Alkanesulphenyl bromides, 270
Alkanesulphenyl chlorides, reaction with phenols, 277
—, chloro-, reaction with cyclohexanone, 277
Alkanethiosulfonic acids, salts, reaction with *o*-nitrobenzenesulphenyl bromide, 344
—, esters, as selective solvents, 334
Alkanethiosulfuric acids, derivs., 325–7
Alkenes. See *Olefins*.
Alkylarsenious mercaptides, 296
Alkylating agents, alkyl phosphates as, 305
Alkyl bromides, 29, 45, 49, 50
Alkyl chlorides, 29, 44, 46
Alkyl halides, thiols from, 25–29
Alkyl disulfides, reaction with P, 294
Alkyl sulfides, chloro-, 381
(Alkylthio)tris(*tert*-butylthio)orthosilicates, 320
Allicin, 334
Allyl mercaptan, 17, 25, 67, 111
Allyl sulfide, 111
Allylthiosulfinic acid, allyl ester, as allicin, 334
Aluminum, thioglycolic acid in analysis of, 448
—, trimethyl-, compd. with MeSH, 150
Aluminum chloride, adducts with mercaptans, 113, 114
—, in petroleum desulfurization, 114
Amidoiminothionophosphoric acid, *N,N'*-diethyl-, 303
Amidothionophosphoric acid, esters, 302, 303
—, *N,N*-diethyl-, esters, 303
Amidothionophosphoric acid, *N*-methyl-, esters, 303
Amidothiophosphoric dichloride, *N*-methyl-, 303
Amines, reaction with P₂S₅, 307
Ammonia, in petroleum desulfurization, 127
Ammonium dithiocarbamate, mercaptans from, 31
5-Androsten-17-one, 3β-mercapto-, 33
Aniline, derivs., reaction with S, 284
—, *N,N*-dimethyl-*p*-(*p*-nitrophenyldithio)-, 278
—, *p*-(*o*-nitrophenylthio)-, 283
—, *N*-sulfinio-, 125
9,10-Anthracenebis(disulfide chloride), 277
9,10-Anthracenedimethanethiol, 33, 75
9-Anthracenedisulfide chloride, 277
Anthraquinone, 2-mercapto-, 391
—, 1-(methylsulfinyl)-, 264
1-Anthraquinoneselenenic acid, 263
1-Anthraquinoneselenenyl bromide, 285
1-Anthraquinonesulfenamide, 280, 283
—, 4-amino-, 280
2-Anthraquinonesulfenamide, 280
1-Anthraquinonesulfenic acid, methyl ester, 264
—, and K salt, stability of, 263
—, 4-amino-, K salt, stability of, 263
1-Anthraquinonesulphenyl bromide, addn. to cyclohexene, 276
—, prepn. of, 271

- 1-Anthraquinonesulfenyl bromide, stability of, 271
 —, 4-amino-, stability of HBr salt, 271
 1-Anthraquinonesulfenyl chloride, 270
 —, reaction with amines, 277
 2-Anthraquinonesulfenyl chloride, 270
 1-Anthraquinonesulfenyl halides, 264
 1-Anthraquinonesulfenic acid, and anhydride, 264
 —, reduction of, 271
 9-Anthracenethiol, 26
 Anticorrosion agents, 305
 Antimonous acid, trithio-, esters, 149
 Antimony, mercaptides of, 149, 150
 —, thionalid in detection of, 449
 Antimony trichloride, reaction with mercaptans, 296
 Antioxidants, for lubricating oils, 305
 —, mercaptans as, 166-167
 Arabinose, thio-, 393
 Arsenic, thionalid in detection of, 449
 Arsine, (2-hydroxytrimethylene) bis[bis(2,3-dihydroxypropylthio)-, 296, 384
 Arylenediseleno-sulfides, 270, 271, 273
 Aryleneselenenyl bromides, 271, 273
 Aryleneselenenyl chlorides, 270, 273
 Aryleneselenenyl selenocyanates, 273, 275
 Aryleneselenenyl thiocyanates, 273, 275
 Aryleneselenenyl tribromides, 271
 Aryleneselenocyanates, 271
 Arylenesulfenic acids, esters, 285
 Arylenesulfenyl chlorides, reactions of, 276, 277
 Arylenesulfenyl selenocyanates, 275
 Aurothioglycolic acid, salts, 439
 Aziridine, 2-methyl-, 398
- B**
- B.A.L., 385-388
 Barbituric acid, 5-(2-mercaptoethyl)-5-pentyl-, 455
 Benzaldehyde, *o*-mercapto-, 390
 Benzamide, *N,N'*-[3-hydroxypropylenebis(thiomethylene)]bis-, 386
 Benz[*a*]anthracenethiol, 26
 Benzene, extraction of mercaptans from, 133-137
 —, dichloro-1,3-bis(chlorosulfenyl)-, 269
 —, 1,3-dimercapto-. See *m*-Benzenedithiol.
 Benzenediazonium chloride, reaction with K ethyl xanthate, 31
 Benzenediseleno-sulfide, *o*-nitro-, 271
 1,3-Benzenedisulfenyl chloride, 4,6-dichloro-, 270
 Benzenedisulfide, iminodi-, 278
 Benzenedisulfide amide, *o*-nitro-, 278
 Benzenedisulfide chloride, *o*-nitro-, 278
 Benzenedithiol, hydroxy-, 402

- m*-Benzenedithiol, 74, 112, 269
—, 2,5-dichloro-, 75
—, dimethyl-, 74
—, 4-ethyl-, 74
o-Benzenedithiol, 74
p-Benzenedithiol, 37, 74
Benzenesulfenamide, 271, 280
—, *p*-acetamido-, 280
—, *p*-chloro-, 280
—, 4-chloro-2-nitro-, 280, 281
—, 2,5-dichloro-, 280
—, *N,N*-diethyl-, 280
—, 2,4-dinitro-, 281
—, *o*-nitro-, 281
Benzeneselenenic acid, 2,4-dinitro-, 263
—, *o*-nitro-, 263
—, *p*-nitro-, acetate, 263
Benzeneselenenosulfonic acid, *o*-nitro-, esters, 334
Benzeneselenenyl bromide, 273
—, 2,4-dinitro-, 285
—, *o*-nitro-, 271
Benzenesulfenamide, 2,4-dinitro-, 281
—, *o*-nitro-, 281
[Benzenesulfenanilide, 4-chloro-4'-hydroxy-2-nitro-, 283
—, *o*-nitro-, 283
Benzenesulfenic acid, 264
—, *o*-nitro-, anhydride, 287
Benzenesulfenimide, 281
Benzenesulfenyl bromide, 271
—, *p*-acetamido-, 271
—, 2-benzoyl-4-nitro-, 271
—, 4-chloro-2-nitro-, 270
—, 2,5-dibromo-, 271
—, *o*-nitro-, 280, 334
Benzenesulfenyl chloride, 267, 269, 271
—, reactions of, 273, 274, 276, 331
—, *p*-acetamido-, 269
Benzenesulfenyl chloride,
 p-chloro-, 269
—, 4-chloro-2-nitro-, 276
—, 2,5-dibromo-, 270
—, 2,5-dichloro-, 270
—, 2,4-dinitro-, 270
—, —, reactions of, 276
—, nitro-, 277
—, *m*-nitro-, 270, 280
—, *o*-nitro-, 270, 276
—, *p*-nitro-, 270, 280
Benzenesulfenyl thiocyanate, 272
—, 2,4-dinitro-, 272
—, *o*-nitro-, 272
Benzenesulfinic acid, silver salt, 274, 331
Benzenesulfonic acid, *p*-mercapto-, 410
—, 2,4,6-trimethylthiol, trichloromethyl ester, 290
Benzenesulfonyl chloride, *p*-(chlorosulfenyl)-, 270
Benzenethiol. See *Thiophenol*.
Benzenethiosulfonic acid, phenyl ester, 274, 331
—, trichloromethyl ester, 290
3*H*-1,2-Benzodithiol-3-one, 458
Benzoic acid, *p*-aminothiol-, 2-diethylaminoethyl ester, 400
—, *o*-(chlorosulfenyl)-, 269
—, *m* (and *p*)-mercapto-, 459
—, *o*-mercapto-. See *Thiosalicylic acid*.
Benzonitrile, reaction with P_2S_5 , 307
Benzophenone, 4,4'-dimercapto-, 391
Benzo[*a*]pyrenethiol, 26
p-Benzoquinone, reaction with thioglycolic acid, 444

- Benzothiazole, 2-mercapto-, 121, 399
 2-Benzothiazolesulfenyl halides, 271
 Benzoxazole, 2-mercapto-, 162
 Benzylamine, reaction with sulfenamides, 280
 Benzylidene dimercaptan, 69
 Benzyl mercaptan, 26, 72
 —, mercury deriv., 143
 —, reactions of, 109, 118
 —, *p*-bromo-, 73
 —, α -butyl-, 55
 —, *ar*-chloro-, 73
 —, *p*-chloro- α -phenyl-, 73
 —, *ar,ar*-dichloro-, 73
 —, α -ethyl-, 55, 73
 —, *ar*-hydroxy-, 389
 —, 3-hydroxy-5-methoxy-, 73
 —, α -isopropyl-, 55
 —, α -methyl, 55, 72
 —, *ar*-methyl-, 73
 —, *ar*-nitro-, 72
 —, α -tolyl-, 73
 Benzyl sulfide, 109
 —, derivs., 464
 Biphenyl, 4,4'-bis(benzylthio)-, 270
 —, 4,4'-bis(chlorosulfenyl)-, 270
 —, dimercapto-. See *Biphenyldithiol*.
 4,4'-Biphenyldisulfenyl chloride, 270
 Biphenyldithiol, 37, 75, 270
 Biphenylthiol. See *Thiophenol, phenyl*-.
 Bismuth, mercaptides of, 149–150
 —, thionalid in detection of, 449
 Borine, chloro(2-chlorovinyl)-(octylmercapto)-, 297
 Borine, dichloro(2-chlorovinyl)-, 297
 Borneol, thio-, 37
 —, —, mercury derivs., 144
 Boron tribromide, reaction with mercaptans, 297
 Boron trifluoride, adducts with mercaptans, 110
 Brassidic acid, mercapto-, 455
 Bromine, oxidation of mercaptans by, 124, 125
 Bunte salts, 32, 84, 326
 Butane, 1,4-bis(2-chloroethylthio)-, 275
 —, 2,3-dibromo-2,3-dimethyl-, oxidation of mercaptans by, 125
 1,4-Butanedisulfenyl chloride, 273, 275
 1,2-Butanedithiol, 3,4-dihydroxy-, and tetraacetate, 386
 —, 4-hydroxy-, 386, 402
 1,4-Butanedithiol, 2,3-dihydroxy-, 386
 2,3-Butanedithiol, 70
 —, 2-methyl-, 20
 Butaneselenol, 54
 Butanesulfenamide, 280
 Butanesulfenyl chloride, 1-chloro-, 268
 Butanesulfuric acid, sodium salt, 23
 Butanetellurol, 54
 Butanethiol, hydroxy-, *S*-acetate, 401
 2-Butanethiol, 3-chloro-, 383
 2-Butene, 2,3-dimethyl-, 125
 —, 2-methyl-, mercaptans from, 40
 2-Butene-1-thiol, 33, 67
 —, 3-methyl-, 67
 3-Butene-1-thiol, 67

3-Butene-2-thiol, 2-methyl-, 20
Butyl bromide, reaction with
thiophenol (Na deriv.), 22
tert-Butyldisulfide cyanide,
279
Butyl mercaptan, 18
—, azeotropes of, 58
—, extraction from isoöctane,
136
—, hydrogenation of, 115
—, phys. props. of, 29, 45 ff, 58–
60, 64
—, prepn. of, 21, 25, 38, 39
—, volatility of, 23–24
—, in warfare, 39
—, 4-(decahydro-2-naphthyl)-,
68
—, 3 (and 4)-hydroxy-, 383
—, 2-methyl-, 65
—, 2-phenyl-, 73
—, 4-(1,2,3,4-tetrahydro-2-
naphthyl)-, 68
sec-Butyl mercaptan, 18, 25
—, phys. props. of, 45, 47, 51,
58–60, 64
tert-Butyl mercaptan, 18
—, mercury deriv., 271
—, phys. props. of, 45, 64
—, prepn. of, 20, 25, 39
—, purification of, 148
tert-Butylsulfenamide, *N,N*-di-
methyl-, 271
tert-Butylsulfenyl bromide, 271
tert-Butylsulfenyl chloride, 266
tert-Butylsulfenyl iodide, 266
Butyl sulfide, 21, 23, 24, 29,
123
Butyric acid, aminomercapto-,
463
—, 3-(benzylthio)-3-methyl-2-
ureido-, 466
—, mercapto-, 452, 453
—, 3-mercapto-3-methyl-, 453
—, 3-mercapto-2-oxo-, 455

C

Cadmium, mercaptides of, 148
Cal-Odorant, 166
2-Camphanethiol. See *Borneol*,
thio-.
Camphor, thio-, silver complex
deriv., 148
Camphorimide, reaction with
 P_2S_5 , 307
Carbamic acid, dialkyldithio-,
anhydrosulfide with alkyl
sulfenic acid, 272
—, dithio, derivs., 275
—, thio-, thioglycolic acid
from, 437
Carbon diselenide, 288
Carbon disulfide, trichloro-
methylenesulfenyl chlo-
ride, from, 287
Carbonic acid, trithio-, derivs.,
275
Carbon selenosulfide, 288
Carbon tetrachloride, 288
Carvone, compd. with H_2S ,
21
Catechol, reaction with sul-
fanyl chlorides, 277
Cellobiose, bromo-, mercaptan
from, 25
—, thio-, 393
Cellothiose, 393
Cellulose, reaction with thio-
glycolic acid, 445
Cetyl mercaptan, 25, 27
Chaulmoogric acid, 2-mer-
capto-, 455
Chlorine, oxidation of mercap-
tans by, 125
Chlorodithiolophosphoric acid,
esters, 298, 313
Chlorofluorothionophosphoric
acid, ethyl ester, 312
Chlorosulfonic acid, 124

- Chlorothiolothionophosphoric acid, *O,S*-diethyl ester, 298
 Chlorothionophosphoric acid, esters, 299, 301, 312-313
 Chlorotrithiophosphoric acid, esters, 298, 313
 Cholesterol, reaction with P_2S_5 , 304
 —, thio-, 37, 68
 Cholesteryl mercaptan. See *Cholesterol, thio-*.
 Choline, thioacetate, 400
 Cinnamic acid, 4-hydroxy-3,5-dimethoxy-, choline ester, 392
 Cinnamyl mercaptan, 73
 Cleansing agents, from thiosulfates, 329
 Coal gas, desulfurization of, 113
 Copper, compds. of, in petroleum desulfurization, 146-147
 —, mercaptides of, 145-147
 —, thionalid in detection of, 448
 Corrosion inhibitors, triaryl tri-thiophosphites as, 296
 —, tributyl trithioborate as, 297
 Coumarin, 4-hydroxy-3-mercapto, 382
 Cresol, reaction with sulfenyl chlorides, 277
 Cresylic acid, reaction with P_2S_5 , 305
 Crotonic acid, 2-acetamido-3-methyl-, penicillamine from, 464
 —, 2-benzamido-3-methyl-, penicillamine from, 464
 —, 3-mercapto-, ethyl ester, 455
 —, 3-methyl-2-nitro-, penicillamine from, 464
 Crotyl mercaptan. See *2-Butene-1-thiol*.
 Cyanamide, reaction with thio-glycolic acid, 445
 Cycloheptyl mercaptan, 68
 1,1-Cyclohexanedimethane-thiol, 71
 1,1-Cyclohexanedithiol, 69
 1,2-Cyclohexanedithiol, 71
 Cyclohexaneselenol, 54
 Cyclohexanone, 2-(methylthio)-, 276
 Cyclohexene, addition of sulfenyl halides to, 275
 —, from cyclohexyl mercaptan, 111
 2-Cyclohexene-1-thiol, 68
 Cyclohexyl mercaptan, phys. props. of, 67, 68
 —, prepn. of, 19, 21, 25, 33, 37, 40
 —, thermal decompn. of, 111
 —, 2-alkylthio-, 406
 —, 2-hydroxy-, 402
 —, —, *trans*-, *S*-thioacetate, 383
 —, methyl-, 21, 68
 —, 2,2,6,6-tetramethyl-, 68
 Cyclooctatetrene, addition of sulfenyl halides to, 275
 Cyclopentaneglycine, 1-mercapto-, formation of, 467
 1-Cyclopentene-1-thiol, 68
 Cyclopentyl mercaptan, 25, 67
 —, 2-hydroxy-, 383, 402
 Cysteic acid, 159, 461
 Cysteine, 460, 461
 —, complex and salt formation by, 462
 —, decompn. of, 462
 —, estimation of, 159
 —, mercury derivs., 143
 —, oxidation of, 461

D

- Decamethylene dimercaptan,
52, 53, 69, 71
- 1-Decene, 112
- Decyl mercaptan, 28, 61, 66
—, thermal decompn. of, 112
- Decyl selenol, 54
- Decyl sulfide, 112, 120
- Depilatories, 442
- Desyl mercaptan, 390
- Diamidothiophosphoric acid,
diphenyl-, 307
- Diamidothionophosphoric acid,
N,N-diphenyl-, esters, 303
—, *N,N,N',N'*-tetraethyl-, es-
ters, 303
- 2,2'-Dibenzothiazole, 399
- Dichlorodithiophosphoric acid,
ethyl ester, 312
- Dichlorothiophosphoric acid,
esters, 298
- Dichlorothionophosphoric acid,
esters, 301, 302, 312
- Diesel fuels, additives for, 292,
294, 295
—, S compds. in, 109
(Difluoromethylene) bis[sulfur
trifluoride], 266
(Difluoromethylene) disulfur
trifluoride pentafluoride,
266
- Difluorothionophosphoric acid,
esters, 312
- β,β -Diglucosyl sulfoxysulfide,
octaacetate, 393
- Diimide, 1-phenyl-2-(tri-
phenylmethylthio)-, 280
- Dimercaptans, 40–43
—, association of, 52
—, *gem*-, 40, 41
—, phys. props. of, 52, 53
- Di(methylthio)bis(phenylsul-
fonyl) orthocarbonate, 319
- Diols, 52, 53
- 4,12-Dioxa-1,7,9,15-tetrathia-
8-stannaspiro[7.7]penta-
decane, 323
- 1,3-Dioxolane, 4,4'-(dithiodi-
methylene) bis[2,2-di-
methyl-, 384
- Diselenides, aryl, 270, 271, 273
- Dispersing agents, from thio-
sulfates, 329
- Disulfide, alkyl chloromethyl,
273
—, alkyl 2,4-dinitrophenyl, 274
—, 9-anthryl *p*-nitrophenyl,
278
—, bis(2-benzothiazolyl), 271
—, *tert*-butyl naphthyl, 273
—, bis(2-chloroethyl), 268
—, bis(3-chloropropyl), 269
—, bis(dialkoxyphosphino-
thiyl), 306, 319
—, bis(diethoxyphosphino-
thiyl), 298
—, bis(trichloromethyl), 290,
292
—, bis(trifluoromethyl), 266
—, bis[tris(*tert*-butylthio)-
methyl], 290
—, bis[tris(ethylthio)methyl],
290
—, bis[tris(propylthio)-
methyl], 290
—, di-*tert*-butyl, 294
—, diethyl, 293
—, iminobis[*p*-nitrophenyl, 278
—, *o*-nitrophenyl phenyl, 273
—, *p*-nitrophenyl *p*-tolylsul-
finyl, 278
- Disulfide chlorides, 277
- Disulfides, addition of halogens
to, 270, 332
—, Alkyl, formation of, 28, 29
—, Bunte salts from, 326
—, cyclic, chlorination of, 269

- Disulfides*, effect on petroleum fuels, 130
 —, from Grignard reagents, 37
 —, isomerism with thiosulfenic esters, 284
 —, mercaptans from, 17, 36
 —, from mercaptans, 118–126
 —, from petroleum wash-liquors, 141
 —, from sulfenamides, 282
 —, sulfenic acids from, 265
 —, from sulfenic anhydrides, 287
 —, from sulfenic esters, 286
 —, from sulfenyl chlorides, 273
 —, sulfenyl halides from, 267
 —, from sulfenyl thiocyanates, 272
 —, thiosulfates from, 326
 —, from thiosulfates, 328
 —, thiosulfinic esters from, 334
Disulfoxides, formation of, 286, 332
 —, identity with thiosulfonic acids, 330
 —, reactions of, 333
 —, structure of, 332
 1,4,2,5-Dithiadiazine, 2,2,5,5-tetrachloro-2,3,5,6-tetrahydro-2,5-di-*p*-tolyl-, 292
p-Dithiane, 379
 —, 2,5-dimethyl-2,5-endoxy-, 390
o-Dithiane-3,6-dicarboxylic acid, 458
p-Dithiane-2,5-dione, 438
 1,3-Dithia-2-silacyclopentane, 320
 1,3,2-Dithiastibiole, 2-chloro-, 296
 Dithiolophosphoric acid, esters, 299, 300, 302, 316
 Dithiolothionophosphoric acid, esters, 300, 316
 Dithionopyrophosphoric acid, esters, 306
 Dithioöorthosilicic acid, *S,S'*-ethylene diester, diethyl ester, 321
 Dithiophosphinic acid, dialkyl-, 308
 —, ethylphenyl-, ethyl ester, 308
 Dithiophosphonous acid, phenyl-, diethyl ester, 308
 Dithiophosphoric acid, derivs., 298
 Dithiopyrophosphoric acid, esters, 303, 318–319
 Djenkolic acid, 462
 Doctor process, 152–155
 Doctor test, 157
 Dodecamethylene dimercaptan, 52, 53, 69
 6-Dodecanethiol, 66
 Dodecyl mercaptan, oxidation by KOH, 129
 —, phys. props. of, 66
 —, prepn. of, 28, 38
tert-Dodecyl mercaptan, 67
 Dulcitol, 1,6-dithio-, 387
 Dyes, from trichloromethanesulfenyl chloride, 292
- E**
- E 605, 309
 Elaidic acid, mercapto-, 455
 Ergothioneine, 467–469
 Erythritol, 1,4-dithio-, 387, 402
 Ester-chlorides, addn. of S to, 298
 Ethane, 1,2-dibromo-1,1,2,2-tetrachloro-, 125
 Ethanedisulfide chloride, 2-chloro-, 278
 1,2-Ethanedithiol. See *Ethylene dimercaptan*.

- Ethanesulfenic acid, 264
—, 1-chloro-, 4-chlorobutyl ester, 285
Ethanesulfenyl chloride, 267, 273
—, 1-chloro-, 268
—, 2-chloro-, 268, 275, 278
—, 1 (and 2)-chloro-1-methyl-, 268
—, 1-chloro-1-phenyl-, 269
—, 1,1-dichloro-, 288
Ethanesulfenyl thiocyanate, 272
Ethanesulfonic acid, 124
—, 2-amino-1-mercapto-, derivs., 401
—, 2-mercapto-, condensation product with *N*-(hydroxymethyl) lauramide, 401
—, —, and derivs., 400
Ethanesulfuric acid, 22
Ethanethiol. See *Ethyl mercaptan*.
Ethanethiosulfonic acid, 331
Ether, bis(2-mercaptoethyl)-, and Ge and Ni derivs., 380
Ethers, mercapto-, 403
Ethyl alcohol, 2,2'-ethylenedithio-, 395
—, mercapto-. See *Ethyl mercaptan*, *hydroxy*-.
—, 2,2'-pentamethylenedithio-, 395
—, 2,2'-tetramethylenedithio-, 395
—, 2,2'-[thiobis(ethylenethio)] bis-, 35
Ethylamine, 2,2'-thiobis-, 398
Ethyl chloride, ethyl mercaptan from, 25
Ethyl chlorophosphite, 48
Ethyl disulfide, 268, 330
Ethylene, addition of sulfenyl halides to, 275
Ethylene, reaction with H_2S , 19-21
—, tetrachloro-, 125
Ethyleneboronic acid, 2-chloro-, dimethyl ester, 297
Ethylene dimercaptan, 41, 42, 52, 53, 69, 70
—, polymers from, 42
—, prepn. of, 25, 42
—, trialkyl trithiophosphites from, 295
Ethylene oxide, reaction with PCl_3 and S, 299
—, reaction with sulfenyl chlorides, 285
Ethylene sodium thiosulfate, reaction with sodium tetrasulfide, 329
Ethyl mercaptan, adducts of, 109
—, azeotropes of, 57, 58
—, bismuth deriv., 150
—, copper deriv., 145
—, decompn. by light, 110
—, discovery of, 15, 16
—, hydrate of, 109
—, as insecticide, 167
—, mercury deriv., 143
—, occurrence of, 16, 17, 18
—, odor of, 16, 166
—, oxidation of, 124
—, phys., props. of, 29, 45, 47, 49ff, 57ff
—, physiol. props. of, 163-165
—, prepn. of, 19, 21, 22, 24, 25ff, 35, 36, 38, 40
—, reaction with ethanesulfenyl chloride, 273
—, in separation of Pt metals, 162
—, sodium deriv., 119, 128
—, solubility of, 131ff
—, surface tension of, 55

Ethyl mercaptan, thermal decomposition of, 111, 116
 —, alkoxy-, 381, 382, 403, 404
 —, 2-alkylamino-, 407
 —, 2,2'-alkyliminobis-, 409
 —, alkylthio-, 406
 —, 2-amino-, 396, 398
 —, —, applications of, 400
 —, —, derivs. of, 399
 —, —, oxidation of, 119
 —, —, phys. props. of, 407
 —, —, reactions of, 399
 —, 2-anilino-, 397
 —, 2-bromo-, 381
 —, butoxy-, 381, 403
 —, 2-(butylamino)-, 397
 —, 2,2'-(butylimino) bis-, 397
 —, 2-chloro-, 380, 381, 405
 —, 2-(2-chloroethylthio)-, 381
 —, 2-cyclohexyl-, 68
 —, dialkylamino-, 408
 —, 2-(dibutylamino)-, 397
 —, 2-[2-(dibutylamino)ethylthio]-, 397
 —, 2,2-diethoxy-, 403
 —, 2-(diethylamino)-, 397, 398
 —, 1,1-dimethyl-2-piperidino-, 397
 —, 1,2-diphenyl-, 73
 —, ethoxy-, 403
 —, 2,2'-(ethylenedithio) bis-, 42
 —, 2-ethylthio-, 394
 —, 2-fluoro-, 381
 —, 2-halo-, 405
 —, 1-hydroxy-, ethers of, 377
 —, 2-hydroxy-, 53, 380, 401
 —, —, and derivs., 377–380
 —, —, polymers from, 379
 —, 2-(2-hydroxyethylthio)-, 379
 —, 2-iodo-, thioacetate, 381
 —, 2-isopropoxy-, 403
 —, 2,2'-oxybis-, 404
 —, 2-phenoxy-, 381

Ethyl mercaptan, 2-piperidino-, 408
 —, 2,2'-thiobis-, 35, 42, 395, 406
 Ethylmercaptomercury salts, 144
 Ethyl nitrite, ethyl mercaptan from, 24
 —, reaction with mercaptans, 293
 Ethyl orthoformate, reaction with P_2S_5 , 306
 Ethyl potassium thiosulfate, 325
 Ethyl selenol, 54
 Ethyl sulfide, 29, 111, 273
 Ethyl tellurol, 54
 Ethyl trisulfide, 123

F

Flotation agents, from benzyl mercaptan, 307
 —, bis(dialkoxyphosphinothioyl) disulfides as, 306
 —, mercaptans as, 168
 —, P_2S_5 reaction products as, 305
 —, from thiosulfates, 330
 1-Fluorenesulfonyl bromide, 9-oxo-, 271
 9-Fluorenone, 1-mercapto-, 271
 Fluorodithiophosphoric acid, esters, 299, 313
 Fluorothionophosphoric acid, diethyl ester, 312
 Fluorophosphorous acid, ethyl ester, 298
 Formaldehyde, reaction with H_2S , 41
 —, reaction with thiosulfuric acid, 325
 Formic acid, reaction with thioglycolic acid, 444

Frasch process, 146
Fructose, thio-, 393
Fuel gas, S compds. in, 109
2-Furanpyruvic acid, α -thio-, 455
Furfuryl mercaptan, 68
—, 5-methyl-, 68
Furoic acid, 5-mercaptomethyl-, 455

G

Galactose, thio-, 393
—, trithio-, 393
Galein, dithio-, 389
Glucocheirolin, 392
Gluconasturtin, 392
Glucose, reaction with thioglycolic acid, 444
—, isopropylidene-6-thio-, 394
—, thio-, 29, 393
—, β -thio-, 391–393
—, 3-thio-, and tetraacetate, 394
Glucosides, thio-, 392
Glucothiose, 391ff
Glucotropacolin, 392
Glutaric acid, 2-methyl-, 457
Glutathione, reduced, mercury derivs., 143
Glycerol, dithio-, 388, 401, 402
—, 1,2-dithio-, and derivs., 385–388
—, 1,3-dithio-, 384–385
—, thio-, 383ff
—, trithio-, 43, 71, 383
Glycolic acid, seleno-, 438
Glycols, dithio-. See *Dimercaptans*.
Glycoses, thio-, 393
Glyoxal, methyl-, reaction with thioglycolic acid, 444

Gold, mercaptides of, 150
—, thionalid in detection of, 449
Grignard reagents, mercaptans from, 37–38
—, reaction with P compds., 308
—, reaction with sulfenic esters, 286
—, reaction with thiosulfonates, 333
—, reaction with trichloromethanesulphenyl chloride, 290
Guanidine, ethyl-, 33

H

Halogens, addn. to disulfides, 332
—, oxidation of mercaptans by, 124–126
Hemiacetals, 377
Hemimercaptals, 394
7-Heptadecanethiol, 67
Heptamethylene dimercaptan, 52, 53, 69
4-Heptanethiol, 66
—, 2,6-dimethyl-, 66
Heptyl mercaptan, 25, 45, 49, 50, 52, 59–61, 65
sec-Heptyl mercaptan, 25, 45, 47, 51, 59–61, 65, 66
Hexadecyl mercaptan, 67
Hexamethylene dimercaptan, 52, 53, 69, 70
1,1-Hexanedithiol, 3,5,5-trimethyl-, 69
1,2-Hexanedithiol, 71
—, 3,4,5,6-tetrahydroxy-, 387
3-Hexanethiol, 20, 65
Hexanoic acid, 6-benzamido-2-mercapto-, 463
—, 4-mercapto-, 454

- Hexyl mercaptan, 25, 45, 47,
49, 50, 52, 59, 60, 61,
65
—, 2-ethyl-, 66
—, 2,3,4,5,6-pentahydroxy-.
See *Sorbitol, 1-thio*-.
sec-Hexyl mercaptan, 25, 45,
47, 51, 59, 60, 65
Homocysteine, 462
Hydantoin, thio-, thioglycolic
acid from, 437
Hydrazine, 1,1,2,2-tetrakis
(phenylthio)-, 281
Hydroascorbic acid, reaction
with thioglycolic acid, 444
Hydrocarbons, aromatic, alky-
lation by mercaptans,
110
—, phys. props. of, 45–52
—, reaction with P_2S_5 , 307
Hydrocinnamaldehyde, γ -mer-
capto-, 407
Hydrocinnamic acid, α (and β)-
mercapto-, 454
—, α -mercapto-2,4,5-tri-
methyl-, 445
Hydrogen fluoride, reactions
with mercaptans, 109, 110
Hydrogen sulfide, compd. with
carvone, 21
—, manuf. from mercaptans in
petroleum, 18
—, mercaptans from unsatd.
hydrocarbons and, 18–21
—, reaction with acetylene,
21
—, reaction with ethylene, 19–
21
—, reaction with ketones (un-
satd.), 21
Hydroxylamine, reaction with
disulfoxides, 333
Hypochlorites, in petroleum de-
sulfurization, 126
- I
- 5-Imidazolethiol, 4-phenyl-,
396
Imides, reaction with trichloro-
methanesulfonyl chloride,
292
—, from sulfonyl chlorides, 280
Inhibitors, mercaptans as, 166–
167
Iodine, oxidation of mercaptans
by, 124
Iron, compd. with dimethyl thi-
olophosphate, 300
—, mercaptides of, 148–149
—, thioglycolic acid in detec-
tion of, 448
Isatin, 158
Isethionic acid, 462
Isoamyl mercaptan. See *Iso-
pentyl mercaptan*.
Isoandrosteryl mercaptan, de-
hydro-. See *5-Androsten-
17-one, 3 β -mercapto*-.
Isobutene, from *tert*-butyl mer-
captan, 20
—, reaction with H_2S , 20
Isobutylene dimercaptan, 42
Isobutyl mercaptan, alkoxy-
derivs., 382
—, prepn. of, 22, 38
—, occurrence of, 18
—, phys. props. of, 45, 58, 64
Isobutyric acid, K salt, as solu-
tizer, 139
—, β -mercapto-. See *Propio-
nic acid, 3-mercapto-2-
methyl*-.
Isooctane, extraction of mer-
captans from, 135, 136
Isooctyl mercaptan, 66
tert-Isooctyl mercaptan, 20
Isopentyl mercaptan, azeo-
tropes of, 59

Isopentyl mercaptan, formation of, 17
—, phys. props. of, 45, 59, 65
—, prepn. of, 22, 25, 26, 38
—, thermal decompn. of, 116
Isopropyl mercaptan, occurrence of, 16, 18
—, from propyl mercaptan, 111
—, phys. props. of, 45, 47, 51, 57, 59, 60, 64
—, prepn. of, 25, 40
Isopropyl selenol, 54
Isopropylsulfenyl chloride, 267
Isothiourea, derivs., tetra-
thioöρθocarbonates from, 319
—, 2-methyl-, 33
Isothiuronium iodide, *S*-alkyl-, 32

K

Ketene, reaction with 4-chloro-2-nitrobenzenesulfenyl chloride, 276
Ketones, reaction with H_2S , 21, 41
—, reaction with sulfenamide, 283
—, reaction with thioglycolic acid, 444
—, mercapto-, 407

L

Lactic acid, 3,3'-dithiodi-, 455
—, 3-mercapto-, ethyl ester, 455
Lactose, thio-, 393
Lauric acid, 129
Lauryl mercaptan. See *Dodecyl mercaptan*.
Lead, mercaptides of, 151–155
—, salts of thiolothionophosphoric acid, 318

Lead sulfide, in petroleum desulfurization, 153–155
Lead tetraethyl, 129, 130
Lewisite, 385
Lignin, reaction with thioglycolic acid, 445
Lubricants, pressure, 305
—, —, bis (dialkoxy-phosphinothiyl-) disulfides in, 306
—, —, diphenyl diamidothiophosphoric acid in, 307
—, —, ethyl (trichloroacetyl) thioglycolate in, 445
—, —, phenyl thiohypophosphate in, 299
—, —, phosphonic triamide derivs. in, 303
—, —, tripentyl and triphenyl trithiolophosphate, 302
Lubricating oils, additives for, 295, 305
—, *S* compds. in, 109

M

Maleic acid, mercapto-, 457
Malic acid, (mercaptomethyl)-, 457
—, 2-mercapto-3-methyl-, 457
Malonamide, bis (chlorosulfenyl)-, 269
—, (chlorosulfenyl) methyl-, 269
Malonic acid, ester, reaction with $RSCl$, 277
—, reaction with thiosulfate esters, 334
Maltose, thio-, 393
Mannitol, 1,6-dithio-, 387, 402
Mannose, thio-, 393
Markownikow's rule, 21, 30
Melissyl mercaptan, 25, 67
Mercaptals, 40, 108, 377, 379
—, cyclic, 43

- Mercaptan. See *Ethyl mercaptan*.
- Mercaptans, 15ff
- , adducts of, 109–110
 - , in alcoholic fermentation, 17
 - , alkoxy-, 403–405
 - , as alkylating agents, 110
 - , AlCl_3 adducts of, 113–114
 - , amperometric titration with I_2 , 266
 - , association of, 47, 54
 - , azeotropes with hydrocarbons, 57, 58
 - , characteristic derivs. of, 162–164
 - , comparison with alcohols, 15, 16, 111
 - , decompn. of, 110–115
 - , detection of, 157–159
 - , dissociation consts. of, 130, 131
 - , effect on petroleum fuels, 129, 130
 - , equilibria with sulfides, 120
 - , estimation of, 159
 - , extraction with aq. alkalies, 131–140
 - , extraction by methanolic NaOH , 137, 138
 - , formation from coal-gas, 38
 - , heats of combustion and formation, 54
 - , identification of, 162, 163
 - , isolation of, 28, 29
 - , metal derivs. of -see *Mercaptides*.
 - , occurrence of, 16–18
 - , odor of, 16
 - , optically active, prepn. of, 24, 25
 - , oxidation of, by halogens, 124–126
 - , oxidation of, by HNO_3 , 120, 121
 - , *Mercaptans*, oxidation of, by O_2 , 118–120, 141
 - , partition consts. in H_2O -hydrocarbon systems, 132–137
 - , in petroleum, 18
 - , phys. props. of, 43–47, 50–52, 54ff
 - , physiol. props. of, 163–165
 - , prepn. of, 18–40
 - , —, from alcohols, 38
 - , —, from aromatic hydrocarbons and S_2Cl_2 , 40
 - , —, from nitriles, 38
 - , —, from olefins, 40
 - , reactions of, 107–261
 - , —, with SbCl_3 , 296
 - , —, with AsCl_3 , 296
 - , —, with BBr_3 , 297
 - , —, with POCl_3 , 298
 - , —, with P_2S_5 , 306
 - , —, with sulfenyl chlorides, 273
 - , —, with sulfenyl thiocyanates, 272
 - , solubilities of, 49, 131
 - , —, in alkaline solutions, 131–140
 - , solvent extraction from petroleum, 155, 156
 - , spectra of, 55, 56
 - , strength of C-S bond in, 111
 - , substituted, 376ff
 - , sulfenyl halides from, 267
 - , sulfides from, 111, 112
 - , thermal decompn. of, 110–115
 - , thiosulfates from, 325
 - , from thiosulfates, 328, 329
 - , urea adducts, 110
 - , uses (miscellaneous) of, 168, 169
 - , uses of, as intermediates, 165, 166

- Meraptans, uses of*, as odors, 166
—, —, in ore flotation, 168
—, —, as pesticides, 167, 168
—, —, in rubber, 167
—, aldehydo-, 389, 390, 407
—, alkoxy-, 403–405
—, alkylthio-, 394–396, 406
—, amino-, 396–400
—, —, applications of, 400
—, —, phys. props. of, 407–409
—, —, reactions of, 399
—, dihydroxy-, 402
—, halo-, 405
—, hydroxy-, 36, 376–389, 401
—, hydroxyaryl-, 389
—, oxo-, 390, 391, 407
Meraptides, 126ff
—, of alkali metals, 127
—, ammonium, 127
—, of antimony, 149, 150
—, of bismuth, 149, 150
—, of cadmium, 148
—, of cobalt and nickel, 149
—, of copper, 145–147
—, from ethyl thioglycolate, 440
—, of gold, palladium and platinum, 150
—, of heavy metals, 141–155
—, of iron, 148, 149
—, of lead, 151–155
—, of mercury, 142–145, 162
—, —, effect of light on, 143
—, reactions of, with AsCl_3 , 296
—, —, with phosphononitrilic acid, 296
—, —, with thisulfonic esters, 333
—, of silver, 148
—, of sodium, 128, 290
—, of tin, 151, 323
—, of zinc, 148
Meraptum, the term, 15
Merapt acids, 436–508
—, physical props. of, 469–473
—, prepn. of, 454, 455
—, the term, 436
—, amino-, 460–462
2-Meraptethyltrimethylammonium iodide, thioacetate, 31
Meraptoles, 108
Meraptum, the term, 15
Mercury, compd. with dimethylthiolphosphate, 300
—, meraptides of, 142–145, 162, 271
—, salts with thiolothionophosphoric acid, 318
—, thionalid in detection of, 449
Methallyl meraptan. See 2-*Propene-1-thiol*, 2-methyl-.
Methane, bis[(2-chloro-1-chloromethylethyl) thio]-, 384
—, bis(2,3-dichloropropylthio)-, 384
—, bis(ethylsulfonyl)-, 41
—, bis(methylsulfonyl)-, 41
—, bis(methylthio)-, 394
Methanedisulfonic acid, derivs., 334
Methanepertiosulfonic acid, *o*-nitrophenyl ester, 334
Methaneselenenyl chloride, chloro-, 268
Methanesulfenamide, *N,N*-diisobutyltrichloro-, 291
—, trichloro-, derivs., 291
—, trichloro-*N,N*-diethyl-, 291
—, trichloro-*N,N*-dimethyl-, 291
—, trimethyl-, 280
—, triphenyl-, 280

- Methanesulfenanilide, anilino-, 280
 Methanesulfenic acid, 2-chloroethyl ester, 285
 Methanesulfenyl bromide, tri-bromo-, 288
 Methanesulfenyl chloride, 267, 273
 —, chloro-, 267
 —, —, addition to unsatd. hydrocarbons, 275, 276
 —, —, phys. props. of, 268
 —, —, reaction of, with alcohols, 285
 —, —, —, with Grignard reagents, 275
 —, —, —, with mercaptans, 273
 —, —, —, with KSCN, 275
 —, —, —, with Na acetoacetic ester, 277
 —, chlorophenyl-, 269
 —, dichloro-, 268
 —, dichloro-*p*-toluidino-, 292
 —, trichloro-, chlorination of, 288
 —, —, formation of, 268
 —, —, phys. props. of, 288
 —, —, preparation of, 287
 —, —, reactions of, 289, 290–292
 —, —, reduction of, 291
 —, triphenyl-, 270
 Methanesulfenyl cyanide, trichloro-, 290
 Methanesulfenyl dichloride, (methylthio) ester, 267
 Methanesulfenyl iodide, 266
 Methanesulfenyl thiocyanate, thiocyanato-, 275
 Methanesulfenyl trichloride, 268
 Methanesulfinic acid, trichloro-, 289
 Methanesulfonic acid, dichloro-, 290
 Methanesulfonyl chloride, 332
 —, trichloro-, 289
 Methanethiol. See *Methyl mercaptan*.
 Methanethioselenosulfonic acid, *o*-nitrophenyl ester, 334
 Methanethiosulfonic acid, methyl ester, 273
 —, sodium salt, reaction with SCl_2 , 332
 Methanetrisulfonic acid, mercapto-, 290
p-Methoxyphenyltellurium chloride, reaction with methanesulfonyl chloride, 332
 Methyl alcohol, as solutizer for mercaptans, 137, 138
 —, mercapto-. See *Methyl mercaptan, hydroxy*-.
 Methylene dimercaptan, 41, 70, 394
 Methyl mercaptan, BH_3 adduct, 110
 —, decompn. by light, 110
 —, formation of, 26
 —, hydrogenation of, 115
 —, occurrence of, 16–18
 —, phys. props. of, 29, 45, 47, 49, 50, 54, 57, 59, 60, 62
 —, physiol. properties of, 163
 —, prepn. of, 22, 24, 34, 38, 40
 —, sodium deriv., 127
 —, solubility of, 131ff
 —, valence force potential of, 54
 —, amino-, 396
 —, bis(*p*-chlorophenyl)-, 73
 —, cyclohexyl-, 38
 —, cyclopentyl-, 68
 —, dithiobis-, 118

- Methyl mercaptan*, ethylthio-, 394
—, halo-, 405
—, hydroxy-, and derivs., 376, 377
—, methoxy-, 403
—, 3-methylcyclohexyl-, 68
—, 3-methylcyclopentyl-, 68
—, methylenedithiobis-, 394
—, morpholino-, 396
—, piperidino-, 396
—, thiobis-, 394
—, trichloro-, 292, 377
—, trifluoro-, 377
—, —, mercury deriv., 266
—, triphenyl-, 26, 27, 40, 73
Methyl selenol, 54
Methyl sulfide, 29, 54
Methyl tellurol, 54
(*Methylthio*) bis(phenylsulfonyl) (phenylthio) ortho-carbonate, 319
Methyl thiocyanate, 288
Methyl thionitrite, phenylcarbamoyl-, 294
Molybdenum, *O,O*-dialkyl thiolothonophosphates in detn. of, 306
—, thioglycolic acid in detn. of, 448
Molybdenum sulfides, 115
Morpholine, 4-(*p*-nitrophenyl-dithio)-, 278
—, 4,4',4''-thiophosphinylidynetris-, 303
Mustard gas, test for, 395
- N**
- 2-Naphthacyl mercaptan, 390
Naphthalene, and alkyl derivs. reaction with P_2S_5 , 307
Naphthalenedithiols, 75
1-Naphthalenedisulfide chloride, 277
2-Naphthalenesulfonyl chloride, 269
2-Naphthalenesulfonyl thiocyanate, 272
2-Naphthalenethiosulfenic acid, 265
2-Naphthol, 1-(*p*-nitrophenyl-dithio)-, 278
Naphthols, reaction with sulfonyl chlorides, 277
Naphthoquinone, reaction with thioglycolic acid, 444
Naphthyl mercaptan, hydroxy-, 403
1-Naphthyl mercaptan, 4-nitro-, 26
2-Naphthyl mercaptan, 269
—, decahydro-, 68
1,1'-Naphthyl sulfide, 111, 115
*Neopentane*tetrathiol, 71, 387
Nickel, mercaptides of, 149
—, salts with thiolothionophosphoric acid, 318
Nitric acid, in oxidation of mercaptans, 120, 121
Nitriles, mercaptans from, 38
—, reaction with thioglycolic acid, 443
Nitrogen mustard, reagents for detection of, 397
Nitroparaffins, sodium derivs., reaction with sulfonyl halides, 275
Nitrosyl chloride, reaction with mercaptans, 292
Nitrous acid, reaction with thio- and dithio-acids, 294
Nonamethylene dimercaptan, 52, 53, 69
5-Nonanethiol, 66
—, 5-propyl-, 67

Nonyl mercaptan, phys. props.
 of, 45, 47, 50–52, 60, 66
 —, prepn. of, 24, 34
sec-Nonyl mercaptan, odor of,
 16
 —, phys. props. of, 45, 47, 51,
 59–61, 66
 —, prepn. of, 27

○

Octadecamethylene dimercap-
 tan, 71
 Octadecyl disulfide, 61
 Octadecyl mercaptan, 25, 28,
 38, 61, 67
 Octamethylene dimercaptan,
 phys. props. of, 52, 53, 69
 2,6-Octanedithiol, 2,6-di-
 methyl-, 71
 —, 3,7-dimethyl-, 84
 2-Octanone, 1-mercapto-, 390
 —, 6-mercapto-7-methyl-, 390
 Octyl mercaptan, phys. props.
 of, 45, 47, 50, 52, 59–61, 66
 —, prepn. of, 25, 34
 —, thermal decompn. of, 111
 —, 4-butyl, 66
sec-Octyl mercaptan, 27, 45, 47,
 51, 59–61
tert-Octyl mercaptan. See *sec*-
Pentyl mercaptan, 2,4,4-
trimethyl-.
 Octyl sulfide, 111
 Oil additives, from olefins and
 P_2S_5 , 307
 Olefins, formation from alkyl
 sulfates, 23
 —, mercaptans from, 18–21, 39,
 40
 —, reaction with P_2S_5 , 307
 Oleic acid, flotation agent from,
 307
 Oleyl mercaptan, 61, 67

Orthocarbonic acid methyl
 ester, from trichlorome-
 thanesulfonyl chloride, 291
 Osmium, thionalid in analysis
 for, 449
m-Oxathiane, 2,2-dimethyl-,
 383
 1,3,2-Oxathiaphosphol-5-one,
 2-chloro-, 446
 1,3-Oxathiolane, 5-chloro-
 methyl-2,2-dimethyl-,
 384
 Oxazolone, derivs., in syntheses
 of penicillamine, 464
 Oxidation of amine and mer-
 captan mixt., 281
 —, of sulfenamides, 283
 —, of sulfonyl halides, 272
 —, thioglycolic acid as inhibi-
 tor of, 447
 —, of thioglycolic acid, 442
 —, of thiolactic acid, 450
 —, of thiosulfates, 329
 —, of trialkyl trithiophos-
 phites, 295
 —, of trichloromethanesulfonyl
 chloride, 289
 Oxidation inhibitors, aryl tri-
 thiophosphates as, 302
 Oxidation-reduction potentials,
 of thioglycolic and thiolac-
 tic acids, 442
 Oxidising agents, for mercap-
 tans, 120–126
 —, sulfenic acids as, 265
 Oxygen, addn. to PCl_3 , 298
 Oxyluminescence, of $PSCl_3$ and
 its derivs., 301

P

Palladium, mercaptides of, 150
 —, thioglycolic acid in analysis
 of, 448

- Palladium*, thionalid in detection of, 449
Parathion, 309–311
Pantothenamide, and *S*-acetyl-deriv., 396
Penicillamine, 463–467
—, *O*-benzoyl-*S*-benzyl-, 464
—, *S*-benzyl-*N*-hexanoyl-, 466
—, isopropylidene-, 466
—, *N*-[*N*-(phenylacetyl)-2-*dl*-glutamyl], 466
7,8-Pentadecanedithiol, 71
8-Pentadecanethiol, 67
Pentaerythritol, tetrathio-. See *Neopentantettrathiol*.
Pentamethylene dimercaptan, 52, 53, 69, 70
1,2-Pentanedithiol, 3,4,5-trihydroxy-, 386
3,3-Pentanedithiol, 69
2-Pentanone, 4-mercapto-4-methyl-, 390
3-Pentanethiol, 65
—, 2,4-dimethyl-, 66
Pentasulfide, bis(*p*-nitrophenyl)-, 278
2-Pentene-1-thiol, 5-alkoxy-, 404
4-Pentene-1-thiol, 67
Pentyl mercaptan, phys. props. of, 29, 45, 47, 49, 50, 52, 59, 60, 61, 64, 65
—, prepn. of, 25, 27
—, 5-cyclohexyl-, 68
—, 5-phenyl-, 73
sec-*Pentyl mercaptan*, 45, 47, 51, 59, 60, 65
—, 4-methyl-, 65
—, 2,4,4-trimethyl-, 66
tert-*Pentyl mercaptan*, 45, 65
Pentyl sulfide, 29
tert-*Pentyl thionitrite*, 293
Perchloromercaptan. See *Methanesulfenyl chloride*, *trichloro*-.
Persulfates, 121
Perylene, 307
Pesticides, mercaptans as, 167, 168
—, trichloromethanesulfenyl chloride in manuf. of, 292
Petroleum, cracking of, 112
—, desulfurization of, 108ff
—, —, by adsorbents, 156, 157
—, —, by alkalis, 129–141
—, —, NH_3 in, 127
—, —, catalysts for, 112–115
—, —, doctor treatment for, 152–155
—, —, by fractionation, 157
—, —, by freezing, 157
—, —, heavy metal salts in, 142ff
—, —, by hydrogenation, 115–118
—, —, led compds. in, 152–155
—, —, phys. methods of, 155–157
—, —, by solvent extraction, 155, 156
—, mercaptans in, 18, 108, 109
—, “platforming” of, 117
—, sulfur compds. in, 18
—, wash liquors from, 140, 141
Phenacyl bromide, reaction with *Na* thioglycolate, 441
Phenacyl mercaptan, and derivs., 390
Phenethyl mercaptan, 30, 73
—, decompn. by *KOH*, 129
Phenethylsulfonyl bromide, 124
Phenethyl thioacetate, 30
Phenol, *p*-mercapto-, 74
—, *p*-(*p*-nitrophenyldithio)-, 278

- Phenol*, *p*-(*p*-nitrophenylthio)-, 278
 Phenols, mercaptans from, 38
 —, reaction with sulfenyl chlorides, 277
 Phenyl disulfide, 267
 Phenylene dimercaptan. See *Benzenedithiol*.
 Phenylhydrazine, reaction with disulfoxides, 333
 Phenyl iodochloride, 125
 Phenylsulfenyl chloride. See *Benzenesulfenyl chloride*.
 Phenyl sulfide, 26, 115
 Phosgene, reaction with thiolothionophosphates, 306
 Phosphine, dichloro (ethylthio)-, 294
 Phosphine, triethyl-, reaction with S, 308
 Phosphine, triphenyl-, reaction with S, 308
 Phosphinic acid, alkyl-, esters, addition of S to, 309
 Phosphoric acid, as catalyst in mercaptan decompn., 112
 —, esters, as alkylating agents, 305
 Phosphorous acid, esters, reaction with P_2S_5 , 295
 Phosphorus oxychloride, reaction with mercaptans, 298
 Phosphorus pentachloride, 125
 —, reaction with H_2S and thio-phosphates, 298
 —, reaction with thiosulfates, 329
 Phosphorus pentasulfide, reactions of, with alcohols, 39, 304
 —, —, with alkenes, mercaptans from, 32
 —, —, Grignard reagents, 308
 —, —, with mercaptans, 306
 Phosphorus sulfochloride, reaction with Grignard reagents, 308
 Phosphorus trichloride, addn. of O, S and Se to, 298
 —, reactions with mercaptans, 294
 —, reactions with thiosulfates, 329
 Phthalimide, reaction with trichloromethanesulfenyl chloride, 292
 —, *N*-(2-bromoethyl)-, 396
 —, *N*-(*p*-nitrophenyldithio)-, 279
 Pickling baths, inhibitors for, 166, 305
 2,5-Piperazinedione, 3,6-divinyl-, reaction with H_2S , 19
 Piperidine, 1,1',1''-thiophosphinylidynetris-, 303
 1-Piperidinecarbodithioic acid, polymethylene esters, dithiols from, 42
 1-Piperidineethanethiol, α,α -dimethyl-, 397
 Plasticizers, for neoprene-type materials, 305
 "Platforming" process, 117
 Platinum, mercaptides of, 150
 —, thionalid in detection of, 449
 Polymercaptans, 43
 Polysulfides, 306
 Potassium cyanate, addn. to thioglycolic acid, 443
 Propanedithiol, 69, 70
 —, hydroxy-. See *Glycerol, dithio*-.
 1,2-Propanedithiol, 3-alkoxy-, 404
 —, 3-amino-, 400

- 1,3-Propanedithiol, 2-amino-2-methyl-, 400
—, 2,2-bis(hydroxymethyl)-, 387
—, 2,2-bis(mercaptomethyl)-. See *Neopentanedithiol*.
—, 2,2-dimethyl-, 70
Propanesulphenyl chloride, 267
—, 1-chloro-, 268
—, 3-chloro-, 269
Propanesulfonic acid, 2-hydroxy-3-mercapto-, metal derivs., 400
—, 3-mercapto-, and derivs., 400
2-Propanethiol, 1-dimethylamino-, 119
—, 2-hydroxy-, 382
—, 1-phenyl-, 73
1,2,3-Propanetrithiol. See *Glycerol, trithio*-.
Propene, from propyl mercaptan, 111
—, reaction with H_2S , 19
Propenedithiol, 42
2-Propene-1-thiol, 2,3-diphenyl-, 73
—, 2-methyl-, 33, 67
Propionaldehyde, 2-(benzylthio)-2-methyl-, 465
—, 3-mercapto-, 407
—, —, thioacetate, 391
—, 3-mercapto-1 (and 2)-methyl-, 407
Propionamide, 2-benzoyl-*N*-(2-mercaptoethyl)-2-methyl-, 397
Propionic acid, 3,3'-[(*p*-acetamidophenyl) arsylenedithio]bis-, 452
—, 2,3-dimercapto-, *S,S*-diacetate, Me ester, 456
Propionic acid, 3,3'-[(*p*-dimethylaminophenyl) arsylenedithio]bis-, 452
—, 2-mercapto-. See *Thiolactic acid*.
—, 3-mercapto-mercaptides and salts from, 451
—, —, oxidation of, 452
—, —, as photographic desensitizer, 447
—, —, phys. props. of, 451
—, —, prepn. of, 451, 452
—, 3-mercapto-2-(mercaptomethyl)-, 456
—, 3-mercapto-2-methyl-, 452, 453
—, 3-(methylthio)-2-(methylthiomethyl)-, 456
—, 2-sulfo-, 450
—, 3,3'-thiodi-, 451
—, 2,2'-trithiodi-, 450
Propionitrile, 2-[2-(diethylamino)ethylthio]-, 399
—, 3-mercapto-, 410
Propyl mercaptan, azeotropes of, 57, 58
—, occurrence of, 17, 18
—, phys. props. of, 29, 45, 47, 49, 50, 52, 54, 57, 59, 60, 63
—, prepn. of, 21, 25, 38
—, thermal decompn. of, 111
—, 2 (and 3)-amino-, 396, 397
—, 2-bromo-, thioacetate, 382
—, 3-bromo-, 383
—, 2-chloro-, and thioacetate, 382
—, 3-chloro-, 383
—, 3-chloro-2-hydroxy-, 384, 405, 406
—, 3-(dialkylamino)-, 409
—, 2,3-dichloro-, thioacetate, 384

Propyl mercaptan, dihydroxy-.
See *Glycerol*, thio-.

—, 2,3-epoxy-, 383

—, 3-ethoxy-, 383

—, hydroxy-, 401

—, 2-hydroxy-, and *S*-thioacetate, 382

—, 3-hydroxy-, 378, 382, 383

—, phenyl-, 73

—, 3-phenyl-, 129

—, 3,3'-thiobis-, 395

Propyl selenol, 54

Propyl sulfide, 21, 29

Propyl tellurol, 54

Pyridine, mercaptoalkyl-, 399, 410

2-Pyridinethiol, 396, 410

—, 3,5-diiodo-, 399

—, 5-nitro-, 399

3-Pyridinethiol, 410

Pyruvic acid, 3-(3,4-dimethoxyphenyl)-2-thio-, 455

—, 2-mercapto-, 455

—, 3-phenyl-2-thio-, 455

Q

2-Quinolinethiol, 396, 410

Quinonimine, *N*-(4-chloro-2-nitrobenzenesulfenyl)-, 283

R

Raney nickel, 115

"Reconstructed cresylic acids," 305

Reduction, of sulfenamides, 283

—, of sulfenyl halides, 272, 273

—, of thiodiacetic acid, 437

—, of thiosulfates, 329

—, of thiosulfonic esters, 333

Resins, from chloroalkanesulfenyl chlorides, 277

—, epoxy, reaction with H_2S , 40

—, from sulfenyl chlorides, 277

Resorcinol, reaction with sulfenyl chlorides, 277

—, dithio-. See *m*-Benzenedithiol.

Rhamnose, thio-, 393

Rubber, hydrogenated, reaction with P_2S_5 , 307

S

Salicylic acid, 5-mercapto-, 460

Selenenamides, 281

Selenenyl halides, reactions with Grignard reagents, 275

Selenium, addn. to phosphites, 300

—, addn. to PCl_3 , 298

—, bis(methylsulfonylthio)-, 332

Selenomercaptans. See *Selenols*.

Selenols, 37, 54

—, reaction with sulfenyl chlorides, 274

1-Selenonaphthol, 91

Selenophenol, 74

—, alkoxy-, 405

—, *p*-bromo-, 74

—, *p*-chloro-, 74

Selenophosphoryl chloride, 298

Selenosalicylic acid, 460

Seleno-sulfides, dialkyl, 273

Silane, alkoxyhalo-, 320

—, trialkylmercapto-, 321

Silanethiol, trichloromethyl-, 321

—, trimethyl-, 40

- Silica gel, in petroleum desulfurization, 156
- 2-Silico-1,3-dithiolane, derivs., 322
- Silver, compds. with di-Et thiolo-phosphate, 300
- , mercaptides of, 148
- , salts with thiolothionophosphoric acid, 318
- , thionalid in detection of, 449
- Sinalbin, 392
- Sinigrin, 392
- Skunk, odor of, 16, 17
- Sodium, in petroleum desulfurization, 128
- Sodium disulfide, alkyl disulfides from, 36
- Sodium hydrogen sulfide, reaction of, with methyl sulfate, 24
- , —, with org. esters, 26
- , —, with sodium alkyl sulfates, 22, 24
- Sodium hydroxide, in petroleum desulfurization, 129
- Sodium nitroprusside, 158
- Sodium plumbite, 152
- Sodium sulfide, reaction with alkyl sulfates, 23
- Sodium tetrasulfide, reaction with ethylene sodium thiosulfate, 329
- Sodium thiosulfate, mercaptans from, 32
- Solutizers, 137–140
- Sodium trithiocarbonate, 31
- Solvents, selective, alkylthio-sulfonate esters as, 334
- Sorbitol, 1-thio-, 388, 389, 402
- Stabilizers, bis(dialkoxyphosphinothioyl) disulfides as, 306
- , for Diesel oils, 305
- Stabilizers, for lubricating oils, 305
- Stability, of inorg. and org. sulfur acids, 263
- Stearic acid, 2-mercapto-, 454
- Stibine, bis(*o*-carboxyphenylthio-)chloro-, 297
- , tris(*p*-acetamidophenylthio)-, 296
- Stratco process, 154
- Styrene, addition of sulfenyl halides to, 275
- , reaction with H₂S, 21
- Succinic acid, 2,3-dimercapto-, 457
- , mercapto-. See *Thiomalic acid*.
- , (mercaptomethyl)-, 457
- , 2-mercapto-3-sulfo-, 457
- Succinimide, *N*-chloro-, as chlorinating agent, 269
- Sulfenamides, 279–284
- , stability of, 263
- , from sulfenyl chlorides, 277
- Sulfenanilide, 283
- Sulfenic acids, 263–265
- , esters, 274, 284–286
- Sulfenic anhydrides, 287
- , stability of, 263
- Sulfenimides, 24, 280
- Sulfenyl bromides, 282
- Sulfenyl chlorides, 266–269, 272, 273, 277, 282
- Sulfenyl cyanides, 263
- Sulfenyl halides, 107, 265–271
- , reactions with NH₃ and amines, 279
- , reactions with Na derivs. of nitroparaffins, 275
- , stability of, 263
- , sulfinic anhydrides from, 287
- , sulfenic esters from, 284
- Sulfenyl iodides, 159

- Sulfenyl selenocyanates, 285
Sulfenyl thiocyanates, 272-276
—, reactions with amines, 280
—, sulfenic esters from, 285
Sulfide, benzyl phenyl, 275
—, bis(2-chloroethyl), 275
—, bis(dialkoxy-phosphinothioyl), 319
—, bis(2-hydroxyethyl), 378
—, bis(methylthiomethyl), 394
—, bis(trifluoromethyl), 377
—, 2-bromoethyl methyl, 271
—, butyl phenyl, 22
—, 2-chlorovinyl 2,4-dinitrophenyl, 276
—, *p*-dimethylaminophenyl
 m-nitrophenyl, 277
—, 2,4-dinitrophenyl 1-nitroethyl, 275
—, ethyl vinyl, 21
—, methyl phenyl, 277
—, phenyl trichloromethyl, 290
Sulfides, alkyl, 23, 24, 34, 35, 120
—, metallic, mercaptan decompn. over, 111
—, from nitroparaffins, 275
—, from petroleum, 123
—, prepn. of, 107
—, sulfenyl halides from, 267
—, of thiophosphorus acid esters, 318, 319
—, hydroxy-, 277
—, mercapto-, 406
Sulfinic acids, esters, from sulfenic esters, 285
—, mercaptans from, 37
—, from mercaptans, 119
—, reduction of, 332
—, sulfenic acids from, 265
—, from sulfenic anhydrides, 287
—, from sulfenic esters, 285
Sulfonal, 165
Sulfonamides, from sulfenamides, 283
Sulfone, bis(ethylsulfonylmethyl), 41
—, bis-[2-(2-hydroxyethylthio)ethyl], 395
—, bis(methylsulfonylmethyl), 41
Sulfone chlorides, 272, 331
Sulfones, oxo-, reaction with thiosulfate esters, 334
Sulfonic acids, 120, 121
—, mercapto-, and derivs., 400
Sulfonyl chlorides, 36, 37
Sulfoxides, isomerism with sulfenic esters, 284
Sulfur, addn. to PCl_3 , 298
—, addn. to trialkyl and triaryl phosphites, 299
—, detection in petroleum, 158
—, reaction with aniline derivs., 284
Sulfur chlorides, reactions with mercaptans, 126
Sulfur compounds, detn. in petroleum, 161
Sulfur dioxide, petroleum desulfurization by, 156
Sulfur fluorides, (trifluoromethyl)-, 266
Sulfuric acid, in oxidation of mercaptans, 123, 124
—, in petroleum desulfurization, 123, 124
Sulfur oxides, in internal combustion engines, 3
Sulfuryl chloride, 125
- T**
- Tellurium, bis(methylsulfonylthio)-, 332
Telluromercaptans, see *Tellurols*.

- Tellurols, 54
Tetra (cyclohexylthio) orthocarbonates, 319
Tetra (alkylthio) orthogermanates, 323, 324
Tetra (alkylthio) orthostannates, 323, 324
Tetradecyl mercaptan, 67
Tetramethylene dimercaptan, 52, 53, 69, 70
Tetramethylenedisulfenyl chloride, 269
Tetramethylene oxide, reaction with sulfenyl chlorides, 285
1,4,6,9-Tetrathia-5-silaspiro-[4.4]nonane, 321
1,2,4,6-Tetrathiepane, 41
Tetrathiogermanates, 323
Tetrathioörrthocarbonates, 319
Tetrathioörrthosilicates, 320
Tetrathioörrthosilicic acid, bis(ethylene diester), 321
Tetrathiophosphoric acids, esters, 299, 306, 316
Tetrathiostannates, 323
Tetrasulfide, bis(dialkoxyphosphinothioyl), 319
—, bis(trichloromethyl), 290
Tetrasulfides, 126, 273
Thallium, compds. with dimethyl thiolophosphates, 301
Thianthrene, 112
1,3,4-Thiazine-2-thiol, 5,6-dihydro-, 398
Thiaziridine, 2,2-dichloro-, aryl deriv., 292
Thiazolidine, deriv., from cysteine, 462
2-Thiazolidine-4-carboxylic acid, 2-mercapto-5,5-dimethyl-, 466
4-Thiazolidinecarboxylic acid, derivs., 466
2,4-Thiazolidinedione, 2-thio-, 445
4-Thiazolidone, 2-imino-, 445
2-Thiazoline-2-thiol, 398
—, 5-methyl-, 398
Thietane, chlorination of, 269
3-Thietanol, 384
2-Thiiranemethanethiol, 386
Thioacetic acid, esters, mercaptans from, 22
—, —, prepn. of, 29, 391
—, phenethyl ester, 30
—, sodium salt, 29
—, phenyl-, 2-(2-phenylacetamido)ethyl ester, 400
Thioacids, esters, prepn. of, 107–108
Thioarsenious acid, esters, 296
—, tris(*o*-carboxyphenyl) ester, 296
Thiobismuth compounds, 297
Thioboric acid, esters, 297
Thiocaine, 400
Thiocarbonyl fluoride, 266
Thiocholine chloride, and derivs., 397
Thiocitramalic acid, 457
Thiocresol. See *Tolyl mercaptan*.
Thiocyanic acid, esters, mercaptans from, 37
—, —, from sulfenyl chlorides, 274
—, *p*-nitrophenyl ester, 279
Thiocyanogen, 272
Thiodiglycolic acid, 437
Thioglycolamide, 445
Thioglycolanilide, gold deriv., 441
—, prepn. of, 445
—, reaction with aldehydes, 444

- Thioglycolic acid, 436-449
 —, ethyl ester, 269, 440
 —, sodium salt, in bacterial culture medium, 447
 —, —, detoxification of cobra venom by, 447
 —, thioacetate, 445
 —, thiobenzoate, 445
 —, trithiocarbonate, di-Na salt, 25
 Thioglycolic-2-naphthalide.
 See *Thionalid*.
 Thioglycolid, 438
 Thiohypophosphoric acid,
 phenyl ester, formation of, 299
 Thioitamic acid, 457
 Thiolactic acid, 449-451
 —, *S*-acetate, 451
 Thiolactones, 453
 Thiolo phosphites, addn. of S to, 300
 Thiolo phosphonic acid, ethyl-, diethyl ester, 319
 Thiolo phosphoric acid, derivs., 299, 301-303
 Thiolo thionophosphonic acid, cyclohexenyl-, dimethyl ester, 319
 —, phenyl-, *S*-ethyl ester, Na salt, 308
 Thiolo thionophosphoric acid, derivs., 39, 300, 304-306, 313-316, 318
 Thiols. See *Mercaptans*.
 Thiomalic acid, 456
 Thionalid, derivs., 449
 —, detection of metal ions with, 449
 Thionaphthol, 73
 —, nitro-, 74
 1-Thionaphthol, 111
 —, 4-bromo-, 74
 —, 4-chloro-, 74
 2-Thionaphthol, 168
 Thioneine. See *Ergothioneine*.
 Thionitric acid, esters, 292-294
 Thionitrous acid, derivs., 292-294
 Thionophosphinic acid, diethyl-, 308
 Thionophosphonic acid, derivs., 308
 —, carboxymethyl-, triethyl ester, 319
 —, benzyl-, diethyl ester, 319
 —, ethyl-, diethyl ester, 319
 —, isopentyl-, diethyl ester, 319
 Thionophosphorane, trialkyl-, 308
 Thionophosphoric acid esters, 299-302, 314-316
 Thionyl chloride, 125
 Thioöxindole, 460
 Thiophene, derivs., from petroleum, 18, 21, 115, 157
 —, formation of, 21
 —, hydrogenation of, 115
 —, removal from benzene, 157
 —, tetrahydro-, 383
 $\Delta^2(3H)$, α -Thiopheneacetic acid, 4,5-dihydro- α -(2-mercaptopropyl)-5-methyl-dithio-, γ -lactone, 453
 3,4-Thiophenedithiol, 71
 —, tetrahydro-, 1-dioxide, 396
 2-Thiophenepyruvic acid, α -thio-, 455
 Thiophenethiol, 37, 40
 2-Thiophenethiol, 37, 68
 3-Thiophenethiol, 69
 —, 2-ethyl-, 69
 Thiophenol, 21, 26, 36, 38, 40, 71, 112, 304
 —, acidity, const. of, and derivs., 74
 —, amine derivs., 127

- Thiophenol*, association of, 47
—, bismuth derivs., 150
—, mercury deriv., 143
—, oxidation of, 120
—, removal from petroleum, 129
—, thermal decompn. of, 116
—, alkoxy-, 405
—, *o*-allyl-, 72
—, 2-allyl-4-methyl-, 72
—, amino-, 398, 409
—, —, mercaptides of, 399
—, *o*-amino-, 398, 399
—, —, cadmium deriv., 148
—, —, heavy metal derivs., 142
—, 2-amino-4-chloro-, 398, 399
—, bromo-, 72, 74, 118
—, 4-bromo-2-nitro-, 72
—, chloro-, 72, 74
—, chloronitro-, 72
—, 2-chloro-4-phenyl-, 72
—, 2,5-dichloro-, 72
—, *p*-dimethylamino-, 399
—, dinitro-, 32, 72
—, ethyl-, isomers, 40, 71
—, hydroxy-, 389, 390, 402
—, iodo-, 72, 74
—, isopropyl-, 72
—, methoxy-, 74
—, methylsulfonyl-, 72, 74
—, nitro-, 72, 74
—, *m*-nitro-, 31, 32, 36
—, *p*-nitro-, 26, 118
—, *o*-[(*o*-nitrophenyl)amino]-, 284
—, pentachloro-, 389
—, *p*-phenyl-, oxidation of, 118
—, *o*-propyl-, 71
—, 4,4'-thiobis-, 396
—, 2,4,6-trinitro-, 72
Thiophosgene, 291
Thiophosphinic chloride, 307
Thiophosphinous acid, di-phenyl-, 308, 309
—, —, esters, 309
Thiophosphonic acid, ethyl-, dimethyl ester, 309
—, isopentyl-, diethyl ester, 309
Thiophosphonic dichloride, ethyl, 319
—, isobutyl-, 319
—, isopentyl-, 319
—, propyl-, 319
Thiophosphorous acid, diethyl ester, 296
—, trialkyl esters, 295
Thiophosphoric acid, amid-esters, 303
—, esters, 297–319
—, —, mercaptans from, 32
—, —, reaction with selenenyl halides, 275
Thiophosphoric triamide, derivs., 303, 307
Thiophosphoryl chloride, 298, 312, 313
Thiopyrophosphoric acid, derivs., 303
—, esters, 318, 319
Thiosaccharides, 391–394
Thiosalicylaldehyde, 390
Thiosalicylic acid, 269, 458, 459
—, —, thioantimonite, 297
Thiosulfates, 328, 329
Thiosulfenic acids, 265
—, esters (see also *Disulfides*), 263
Thiosulfinic acids, esters, 275, 334, 335
Thiosulfite esters, 335–337
Thiosulfonic acids, derivs., 330–334
—, esters, 269
Thiosulfuric acid, 274, 325, 327
—, alkyl esters, salts—see *Bunte salts*.

- Thiosulfuric acid*, esters, 275, 325
Thiosulfurous acid, esters, 335–337
Thiourea, mercaptans from, 32–35
 —, thioglycolic acid from, 436
Thioxyleneol, 71
Threitol, 1,4-dithiol-, 402
Thymol, reaction with sulfenyl chlorides, 277
Tin, mercaptides of, 151, 323
 —, thionalid in detection of, 449
Toluene, α,α' -(4,6-dichloro-1,3-phenylene)bis-, 270
 3,4-Toluenedithiol, 162
p-Toluenesulfenamide, 2-nitro-, 280
m-Toluenesulfenyl bromide, 4-nitro-, 271
p-Toluenesulfenyl chloride, 276
 —, 2-nitro-, 270
p-Toluenesulfonic acid, mercaptans from esters of, 26
 α -Toluenethiol. See *Benzyl mercaptan*.
ar-Toluenethiol. See *Tolyl mercaptan*.
Toluenethiosulfonic acid, S-butyl ester, 331
 —, trichloromethyl ester, 290
p-Toluidine, *N*-(*p*-nitrophenyl-dithio)-, 278
Tolyl mercaptan, 71
m-Tolyl mercaptan, 74
p-Tolyl mercaptan, 26, 56, 74
 —, 2-hexyl-, 40
 —, 2-nitro-, 73
Tolyl selenol, 74
p-Tolyl trithioantimonite, 45
Tri(alkylthio)orthosilicofor-mic esters, 320
Tri(alkylthio)silane halide, 320
Tributyl trithioborate, 297
Tridecyl mercaptan, 67
 (Trifluoromethyl)sulfur chlo-ride, 266
 (Trifluoromethyl)sulfur penta-fluoride, 265
 (Trifluoromethyl)sulfur tri-fluoride, 266
Trimethylene dimercaptan, 42, 52, 53, 69, 70
 —, 2,2-bis(mercaptomethyl)-, 43
 —, 2,2-dimethyl-, 42
Trimethylenedisulfenyl chlo-ride, 269
Trimethylene sulfide. See *Thi-etane*.
Trimethylsilyl mercaptan, 69
Tripentyl trithiophosphite, as Diesel fuel additive, 295
Triphenyl thioarsenite, 296
Trithiane, 268
Trithioantimonous acid, esters, 296–297
Trithiocarbonic acid, esters, 41, 143
 —, thioglycolate, disodium salt, 31
Trithiometaphosphoric acid, 306
Triselenane, 268
Triselenide, aryl, 271
Trisulfide, acetyl *p*-nitro-phenyl, 278
 —, bis(dialkoxy-phosphino-thi-oyl), 319
 —, bis(methylsulfonyl), 332
 —, bis(trichloromethyl), 290
 —, bis[tris(*tert*-butylthio)-methyl], 290
 —, bis[tris(phenylthio)-methyl], 290
 —, dimethyl, 273
 —, diphenyl, 273

Trisulfide, *o*-nitrophenyl

p-nitrophenyl, 278

Trisulfides, 126, 273

Trithiophosphonic acid,
phenyl-, diethyl ester, 308

Trithiophosphoric acid, esters,
295, 299, 300, 302, 316

Trithiophosphorous acids,
esters, 294–296

U

Undecamethylene dimercaptan,
52, 53, 69

2-Undecanethiol, 2-methyl-, 67

Undecanoic acid, 11,11'-dithi-
odi-, 454

—, 11-mercapto-, 454

Undecyl mercaptan, 66

Unisol process, 138

Urea, adducts with mercap-
tans, 110

—, 1,3-bis(mercaptomethyl)-,
396

—, 1-phenyl-1 (and 3)-*p*-tolyl-
thio-, 280

Uscharin, 389

V

Valeric acid, 2-amino-3-ethyl-
3-mercapto-, 463

—, 2-amino-3-mercapto-, 463

—, 2-amino-3 (and 4)-mer-
capto-4 (and 3)-methyl-,
463

—, 3 (4 and 5)-mercapto-, 453

—, 4-mercapto-4-methyl-, 454

Vinyl mercaptan, 21

W

Walden inversion, of thio-
glycolic acid derivs., 441

Waving preps. for hair, thio-
glycolic acid in, 442

Wash liquors, from petroleum,
regeneration of, 140, 141

Waxes, ester-type, reaction
with P_2S_5 , 307

Wetting agents, formation from
thiosulfates, 329

X

Xanthates, mercaptans from,
30–32

Xanthic acid, derivs., reaction
with sulfenyl halides, 275

—, —, thioglycolic acid from,
437

—, (carboxymethyl)-, dipotas-
sium salt, 445

—, (piperidinophosphinyl-
idyne) di-, diethyl ester,
303

—, thio-, derivs., reaction with
sulfenyl halides, 275

X-radiation, in desulfurization
of petroleum, 110

Xylothiose, 393

Z

Zinc, mercaptides of, 148

Zinc compounds, in petroleum
desulfurization, 114